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PART I

AD0872241

## SYNTHESIS OF MULTIFUNCTIONAL PERFLUOROALIPHATIC ETHER MONOMERS

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TECHNICAL REPORT AFML-TR-70-70, PART I  
July 1970

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AFML-TR-70-70  
PART I

SYNTHESIS OF MULTIFUNCTIONAL  
PERFLUOROALIPHATIC ETHER MONOMERS

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PENINSULAR CHEMRESEARCH

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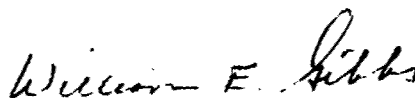
## FOREWORD

This report was prepared by Peninsular ChemResearch, Gainesville, Florida, under Contract No. F33615-69-C-1279, which was administered by the Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Dr. Christ Tamborski is Project Engineer for the Air Force.

This is a final report under this contract and covers the period of 1 March to 30 November, 1969.

Personnel who have contributed to this research are Dr. Paul D. Schuman, Project Director, and Calvin Padgett, Research Chemist. Analyses were carried out under the supervision of Dr. Dale A. Warner, Director of Analytical Services. Drs. George Butler and Paul Tarrant are acting consultants.

This Technical Report has been reviewed and is approved.



---

William E. Gibbs  
Chief, Polymer Branch  
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Ohio

## ABSTRACT

Perfluorostyrene was synthesized and several attempts to prepare perfluorostyrene epoxide were not successful. Perfluoro(polyether diacids), acid fluorides, nitriles and esters were prepared. Perfluoro-p-bromo-octyl benzene was synthesized. A high molecular weight perfluoro(polyether)-substituted s-triazine fluid was prepared.

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 $[\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{CNH}]_2\text{NH}$

Figure 17. An Infrared Spectrum of  
 $[\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{CN}]_3$  s-Triazine Fluid

# TABLES

Table 1. Materials Synthesized and Submitted to the Air Force  
 Materials Laboratory

# GLOSSARY OF TERMS

Throughout this report the following system of nomenclature has been adopted for the following structures:

<u>Name</u>	<u>Structure</u>
sym-DEDAF	$\begin{array}{c} \text{O} & & \text{O} \\ \parallel & & \parallel \\ \text{FC}-\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)-\text{CF} \end{array}$
unsym-DEDAF	$\begin{array}{c} \text{O} & & \text{O} \\ \parallel & & \parallel \\ \text{FC}-(\text{CF}_2)_4\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)-\text{CF} \end{array}$
sym- & unsym-DEDAME	$\begin{array}{cc} \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{OC}- \end{array} & \begin{array}{c} \text{O} \\ \parallel \\ -\text{COCH}_3 \end{array} \end{array}$
sym- & unsym-DEDA	$\begin{array}{cc} \text{HOOC}- & -\text{COOH} \end{array}$
sym- & unsym-DEDAA	$\begin{array}{cc} \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{NC}- \end{array} & \begin{array}{c} \text{O} \\ \parallel \\ -\text{CNH}_2 \end{array} \end{array}$
sym- & unsym-DEDN	$\begin{array}{cc} \text{NC}- & -\text{CN} \end{array}$
DEDAF	mixture of sym- & unsym-DEDAF
PFGF	$\begin{array}{c} \text{O} & \text{O} \\ \parallel & \parallel \\ \text{FC}(\text{CF}_2)_3\text{CF} \end{array}$
HFGCl	$\begin{array}{c} \text{O} & \text{O} \\ \parallel & \parallel \\ \text{ClC}(\text{CF}_2)_3\text{CCl} \end{array}$
HFPE	$\text{CF}_3\overline{\text{CFCF}_2}\text{O}$
MEDAF	$\text{FOC}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)\text{COF}$

## INTRODUCTION

Present and future space requirements have created a critical need for new and improved materials for use in aircraft and missiles. These materials, many of them non-metallic, must function under extreme environmental conditions and serve a variety of purposes. In preparing materials to meet these requirements, particularly polymeric materials, it is necessary to obtain monomers which, on the basis of both empirical and theoretical evidence, can be polymerized to give new materials exhibiting the desired properties. The preparation of new, tailor-made monomers is frequently an expensive and time-consuming process resulting in delays in synthesis and evaluation of the system under study.

In general, replacement of hydrogen with fluorine on a polymer chain results in dramatic changes in properties of the polymer. The fluorocarbon analogs of hydrocarbon polymers exhibit greatly improved thermal, oxidative, and wide spectrum chemical stability. Unfortunately, associated with these beneficial changes in properties is an increase in polymer backbone rigidity with consequent increase in the polymer glass temperature.<sup>1</sup> In order to take advantage of the good high temperature resistance and chemical properties of fluorocarbon polymers, current research is being directed toward the synthesis of polymers containing heteroatoms in the polymer chain. The increase in chain flexibility by the inclusion of sulfur in the polymer chain is evidenced by the low T<sub>g</sub> of poly(thiocarbonyl fluoride)<sup>2</sup> at -118°. In addition, poly(perfluoro-tetramethylene oxide)<sup>3,4</sup> is flexible at -80°, -60°.

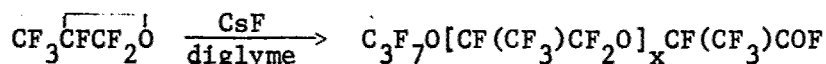
The object of this contract is to synthesize functional aliphatic or aromatic ether monomers which may be used by the Air Force Materials Laboratory in the preparation of thermally and oxidatively stable materials ranging in properties from fluids to elastomers.

## DISCUSSION

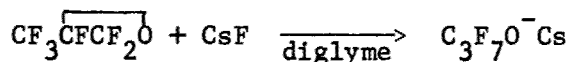
### I. Synthesis of Perfluoropropylene Epoxide Oligomer Acid Fluorides and Derivatives, DEDAF, DEDAME, DEDA and DEDN

One of the most convenient routes to these compounds is that of Fritz, Moore, and Selman<sup>5</sup> in which they found that fluorocarbon polyether acid fluorides could be prepared through oligomerization of hexafluoropropylene epoxide (HEPE). This may be conveniently carried out through fluoride ion initiation in a suitable high dielectric solvent such as acetonitrile or diglyme.

Thus,

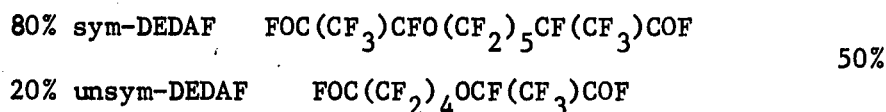
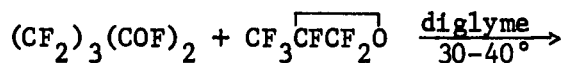
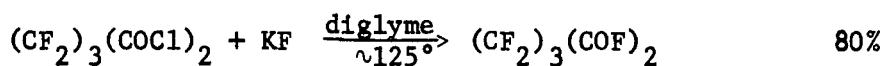


HFPE rearranges in the presence of CsF to yield the attacking species, the heptafluoropropoxide ion.



Fluorocarbon ketones and acid fluorides were also found to react with CsF to give the corresponding fluorocarbon alkoxides. Thus, a wide variety of reaction products may be produced using different initiating species. By varying reaction conditions a reasonable degree of control over product distribution may be exercised.

One of the objectives under this contract was the synthesis of diacids and dinitriles containing two ether oxygen atoms. It was found possible to obtain suitable difunctional acid fluorides in 50% yield through reaction of HFPE with perfluoroglutaryl fluoride at 30-40°. The overall reaction is as follows:

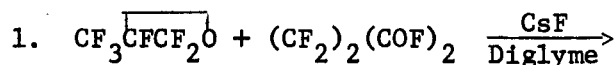


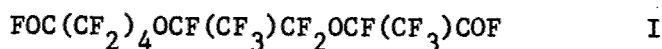
plus

$\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COF}$  and longer chain polyether diacid fluorides.

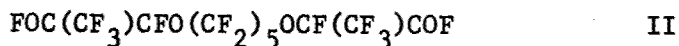
Since these difunctional ethers are to be used in evaluation of new polymer systems, a primary consideration in this synthesis is that of product purity. Unfortunately, the isomeric DEDAF's (dietherdiacid fluorides) or their derivatives are not separable by distillation. No chromatographic stationary phase has been found suitable for this separation. However, the isomeric methyl esters are found to be difficultly separable on an extended preparative GLC column. [80" 20% W-98 (silicone gum rubber) on Prep. grade Chromatoport S plus 80", 10% Carbowax 20M on Chromatosorb G with a column temperature of 125° and injection temperature of 210°.] Infrared spectra of the sym and unsym-DEDAME isomers are shown in Figures 1 and 2.

Because of this difficulty in separation of the isomeric DEDAF's it was considered advisable to carry out some preliminary investigation, at the Air Force Materials Laboratory, using derivatives of the mixed isomers. Several hundred grams of the two isomeric DEDAF's were prepared and from these acid fluorides the corresponding diether diacids and dinitriles were prepared. Thus,

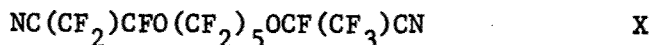
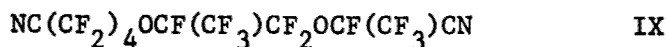
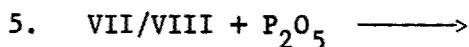
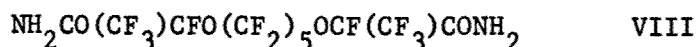
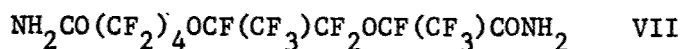
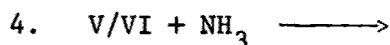
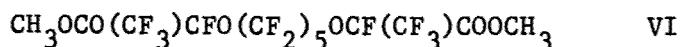
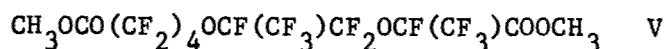
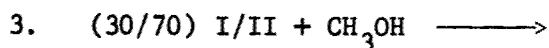
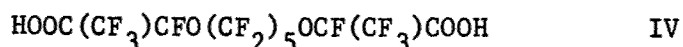
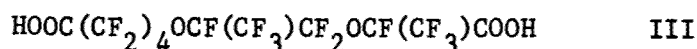
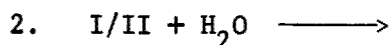




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plus other oligomers and homo oligomers  
of HFPE

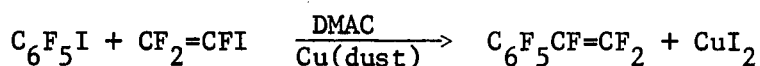


Infrared spectra of the mixed isomer diacids (II/III) and dinitriles (IX/X) are shown in Figures 12 and 13.

## II. Synthesis of Perfluorostyrene

Synthesis of perfluorostyrene was carried out essentially as described by Tamborski<sup>5a</sup> with the exception that the immediate pentafluorophenyl copper was prepared in situ. All reactants were combined,

and the product distilled from the reaction mixture.



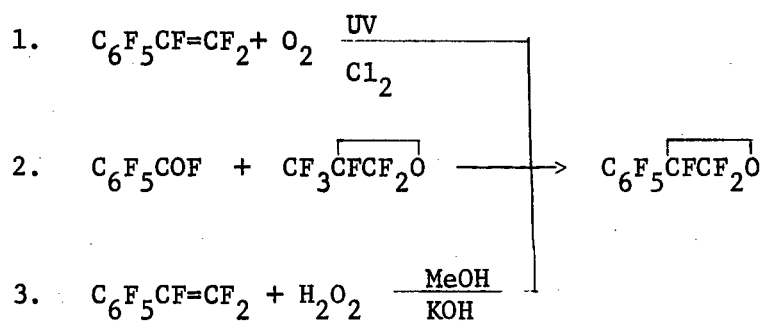
Two small scale trial runs were carried out initially to determine suitable reaction conditions and also to determine the effectiveness of a new copper dust reagent being used. The small scale reactions gave 41 and 25% yields in open and closed systems.

Scale-up to a 1.7 mole run in an open system gave a 28% yield of perfluorostyrene. An infrared spectrum of the distilled product boiling at 121-122° was identical to that of an authentic sample of perfluorostyrene (Figure 3).

### III. Attempted Synthesis of Perfluorostyrene Epoxide

Oligomerization or polymerization of perfluorostyrene epoxide should yield fluids and polymers having good thermal and chemical properties.

Several methods of synthesis of perfluorostyrene epoxide are suggested by literature references. The following three approaches were attempted.



The halogen-UV catalyzed epoxidation of fluoroolefins has been carried out in the synthesis of tetrafluoroethylene oxide<sup>6</sup> and the synthesis of fluorocarbon diepoxides.<sup>7</sup>

In our initial attempt to epoxidize perfluorostyrene with oxygen the reaction was carried out at room temperature with the  $\text{O}_2/\text{Cl}_2$



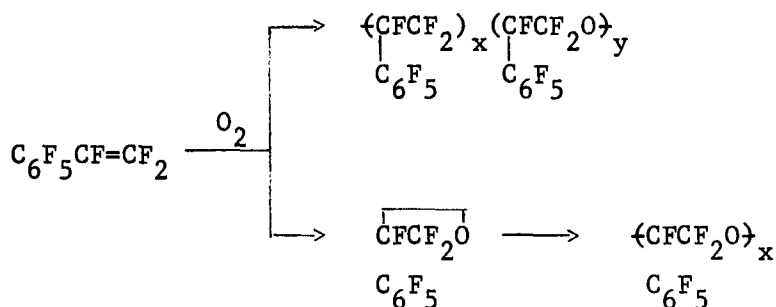
pressure maintained at about 760 mm. Oxygen take-up after 24 hours irradiation was about 62% that calculated for total epoxidation. After 30 hours reaction GLC analysis indicated complete reaction of the styrene. An infrared spectrum of a crude distillation product boiling about 100° showed absorption maxima at 5.3 and 5.45 microns suggesting the presence of fluoroaliphatic and perfluoroaromatic acid fluoride carbonyl groups (Figure 4). Comparative infrared spectra of perfluorobenzoyl fluoride and perfluorostyrene are shown in Figures 5 and 3. In addition there was obtained a high boiling, viscous residue. An infrared spectrum of this product is shown in Figure 6.

The 5.3 micron infrared absorption would suggest epoxide formation and rearrangement to pentafluorophenyl acetyl fluoride. In addition the presence of the apparent polymeric material would further suggest epoxide oligomerization or styrene polymerization was occurring.

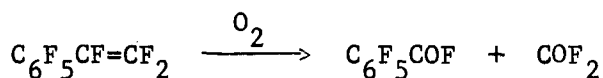
In view of this, it was considered advisable to determine if perfluorostyrene could be polymerized under similar conditions. Irradiation of perfluorostyrene for 72 hours at ambient temperature yielded a viscous, light brown liquid. Upon removal of volatiles, at 100° under vacuum (mostly unreacted styrene) a low melting solid polymer was obtained. An infrared spectrum of this polymer (Fig. 7) shows some similarity to that obtained in the epoxidation attempts but shows a strong maximum at 5.6 microns.

Fair yields of fluorocarbon diepoxides were prepared at PCR under an Air Force contract<sup>7</sup> by bubbling O<sub>2</sub> through the corresponding diene. The high styrene to oxygen ratio and the polymerizability of perfluorostyrene appeared to preclude the success of this approach in the present synthesis.

In view of this it was reasoned that polymerization may be reduced or even eliminated by increasing the oxygen to styrene ratio. Thus, homopolymerization may be initiated but the presence of a high oxygen ratio may interrupt or eliminate polymerization.

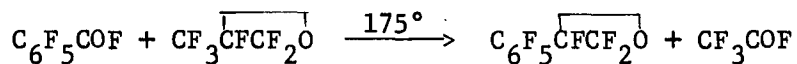


or oxidation to perfluorobenzoyl fluoride may occur.

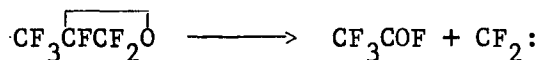


In carrying out this reaction a high oxygen ratio was obtained by adding oxygen, containing about 0.75% chlorine, to a 6-liter, evacuated system containing perfluorostyrene. The lower part of the system was heated to 100° while the upper portion was irradiated with a Hanovia desk U.V. lamp. An initial reflux stopped after about 1.5 hours irradiation and an infrared spectrum of the overgases showed the presence of  $\text{COF}_2$  and  $\text{SiF}_4$ . The remaining reaction mixture, which had darkened, was mainly composed of perfluorobenzoyl fluoride and unreacted perfluorostyrene. No epoxide nor the presence of aliphatic COF was detected.

By analogy to the difluorocarbene addition in the synthesis of tetrafluoroethane<sup>9</sup> it was considered possible to make a similar addition to the carbonyl group in pentafluorobenzoyl fluoride. Thus,



HFPE is reported to decompose at 170° to give trifluoroacetyl fluoride and difluorocarbene.



Our initial attempt was not successful. After heating the

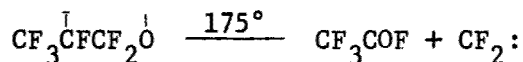
epoxide and acid fluoride at 175° for 48 hours there was no indication of the presence of perfluorostyrene epoxide.

A model reaction was run to determine the extent of decomposition of HFPE at 200°. After 48 hours at this temperature an ampoule containing HFPE was noted to contain white solids. After being removed from the heater and allowed to cool for several minutes the ampoule exploded when jarred slightly. The calculated pressure in the ampoule (>200 psia) was not sufficient to burst the ampoule used. This is especially true if the C<sub>2</sub>F<sub>4</sub> generated in decomposition polymerized to the noted solid.

Although the occurrence of this explosion is reminiscent of poly(tetrafluoroethylene peroxide) detonations, it would appear more reasonable to assume that the ampoule contained some strains. A slight jar apparently was sufficient to initiate rupture of the ampoule.

Seyferth<sup>10</sup> recently prepared epoxides by carbene addition to carbonyl compounds. Seyferth's work and our unsuccessful attempt to epoxidize perfluorostyrene would suggest the second method above, or a modification of this method, as the most promising approach to the synthesis of perfluorostyrene epoxide.

Carbene sources other than that derived from HFPE may be more appropriate since the success of this reaction would depend on the relative thermal stabilities of the two epoxides. Thus, the following equilibria would presumably occur. A greater stability for the aromatic epoxide would be required, as indicated.

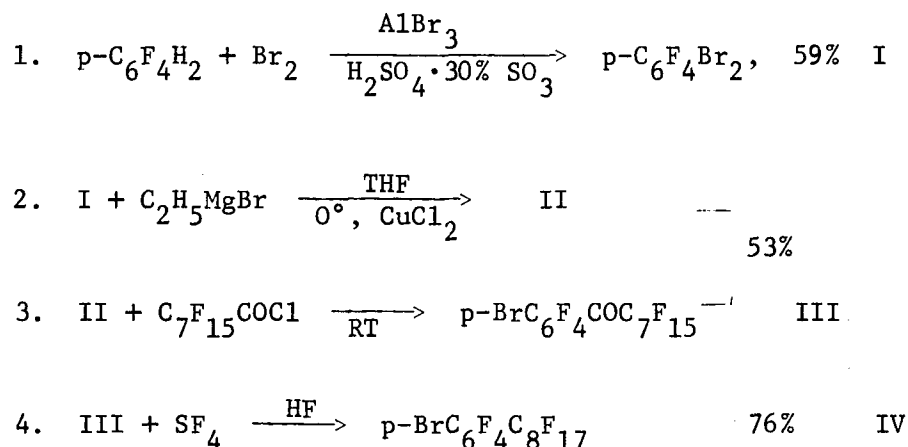


Possibly a better carbene source (as suggested by C. Tamborski, Air Force Materials Laboratory) would be through thermal decomposition of CF<sub>3</sub>Sn(CH<sub>3</sub>)<sub>3</sub>. This organometallic compound decomposes at 150° in the presence of C<sub>2</sub>F<sub>4</sub>, to give a nearly quantitative yield<sup>11</sup> of perfluorocyclopropane. Seyferth<sup>12</sup> found that this decomposition could be carried out as low as 80° in the presence of NaI in glyme.

Reaction 3 was also attempted. Only unreacted starting material was recovered when perfluorostyrene was allowed to react with basic  $H_2O_2$  in methanol/ water at  $-40^\circ$ . Only about half of the unreacted styrene and no identifiable aromatic by-products were recovered.

#### IV. Synthesis of Perfluoro-p-bromo octyl benzene

The method used in the synthesis of the titled compound is that described by Dr. C. Tamborski (letter and note, 9 July 1969). The reaction scheme is as follows:



An overall yield of 23.4% was obtained starting with  $p-C_6F_4H_2$ .

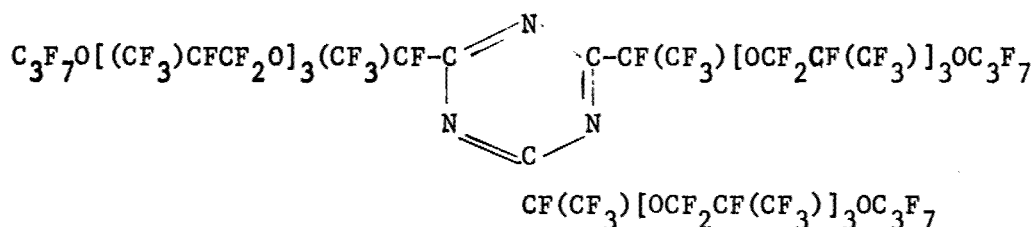
In our first attempt to carry out the final ketone fluorination step using  $SF_4$  with  $AlF_3$  as a catalyst no fluorination occurred. Essentially all of the starting ketone was recovered by distillation. In a second attempt a 76% yield of  $p-BrC_6F_4C_8F_{17}$  was obtained by carrying out the  $SF_4$  fluorination in anhydrous HF. An infrared spectrum is consistent with the structure assigned this compound. This product, 33 g., was sent to the Materials Laboratory.

#### V. Synthesis of $(C_3F_7O[CF(CF_3)CF_2O]_3CF[CF_3]CN)_3$

Technological advances in the fields of aeronautics and astronautics place ever increasing demands on materials of construction as well

as on supporting systems. One area of particular urgency is that of fluids which exhibit useful properties and are stable over wide temperature extremes.

A system which has shown considerable promise as a thermally and oxidatively stable hydraulic fluid is that of the perfluoroalkylether-substituted s-triazines. A number of s-triazine fluids were synthesized at Peninsular ChemResearch under a program with the Bureau of Ships.<sup>13</sup> Of particular interest in this series of fluids was a fluid having the following structure.



This fluid has a mol. wt. of 2577 g/mole, boils at 175-177° at 0.08 mm and has a pour point of -45° F. The estimated boiling point of this fluid at atmospheric pressure is 830° F, indicating a fluid range of 875° F.

Approximately 800 g. of this fluid was synthesized using the following six step reaction.

1.  $\text{CF}_3\text{CF}=\text{CF}_2 + \text{H}_2\text{O}_2 \xrightarrow{32.5\%} \text{CF}_3\text{CFCF}_2\text{O}$  (I)
2.  $\text{I} \xrightarrow[\text{diglyme}]{\text{C}_8\text{F}_8} \text{C}_3\text{F}_7\text{O}[(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n\text{CF}(\text{CF}_3)\text{COF}]$  (II)  
(39% where n=3)
3.  $\text{II} + \text{NH}_3 \longrightarrow \text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CONH}_2]$  (III)
4.  $\text{III} + \text{P}_2\text{O}_5 \longrightarrow \text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CN}]$  (IV)  
(Step 3 and 4, 82%)
5.  $\text{IV} + \text{NH}_3 \longrightarrow \text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{C}(=\text{NH})\text{NH}_2]$  (V)
6.  $\text{V} \xrightarrow{-\text{NH}_3} [\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CN}]]_3$   
(Steps 5 and 6, 94%)

Starting with hexafluoropropene (HFPE no longer commercially available) an overall yield of 9.8% of the desired s-triazine fluid was obtained.

As may be anticipated the oligomerization reaction, step 2, is a low yield reaction. Normally a yield of 20 to 25% of pentamer acid fluoride is obtained. Several experiments were conducted in an attempt to determine degree of oligomerization and product distribution with respect to temperature. The following results were obtained.

$$\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}(\text{CF}_3)\text{COF}$$

Reaction Temperature	Predominant n in product
-15°	no reaction
15°	0, 1, 2, 3
n 55°	0, 1, 2

It was found that by recharging oligomers where n=0, 1 and 2 a predominance of the desired oligomer (n=3) may be obtained. Thus, the following oligomer distribution was obtained when low mol. wt. oligomers were allowed to react with HFPE.

$$\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}(\text{CF}_3)\text{COF}$$

<u>Product Distribution</u>	
n	wt. % of Product
0	0
1	0
2	2
3	54
4	33
> 5	11

## VI. Miscellaneous Reactions

In the synthesis of the DEDAF fluorocarbon diacid fluorides a number of by-product acid fluorides are also obtained. Synthesis of  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{I}$  would be of interest in cross coupling reactions to modify

fluid properties. In addition, the diacid and dinitriles of MEDAF and homologues having mol. wt. greater than DEDAF may be used in the synthesis of new polymers.

Initially an attempt was made to prepare the above iodide by decarboxylation of the acid fluoride in the presence of KI. No apparent reaction occurred at 200°.

A small quantity of the iodide was prepared by the Hunsdiecker Reaction.

## EXPERIMENTAL

### I. Synthesis of DEDAF and DEDAME

#### A. Synthesis of Perfluoroglutaryl Fluoride, PFGF

A 5-liter, 3-neck flask was charged with KF (500 g., 8.62 moles) and heated at 150° under vacuum for 18 hours; it was then cooled and Diglyme (2000 ml.), freshly distilled from sodium, was added. The flask was fitted with a stirrer, an addition funnel containing HFGCl (800 g., 2.84 moles), and a Vigreux column topped with an iced water-cooled distillation head vented to a -183° trap. The reaction flask was heated to ~125° and the perfluoroglutaryl chloride was added at a rate sufficient to allow a convenient distillation of the PFGF. The PFGF, distilling at 45-50°, was found to weigh 565 g. (80% conversion) and was shown to be 98% pure by GLC (6', 15% PFOX/75 on HMDS treated Gas Chrom C1, room temp).

#### B. Reaction of Perfluoroglutaryl Fluoride With Hexafluoropropylene Epoxide

Cesium fluoride (59.2 g., 0.40 moles) and a stirring bar were placed in a 5-liter, 1-neck flask and heated at 150° under vacuum for 18 hours. The flask was cooled and Diglyme (740 ml.), freshly distilled from sodium, was added. The flask was then fitted with an addition funnel containing PFGF (564 g., 2.31 moles) which was added dropwise. A slight exotherm was noted. After the addition of PFGF was completed, the flask was cooled in a water bath and connected to a cylinder of HEPE via a manifold for reading pressures from 0 to 1500 mm.



A pressure of ~1000 mm was maintained as the HFPE (1173 g., 7.07 moles) was bled into the reaction flask. It was necessary to continually add ice to the water bath to maintain a temperature of 30-40°. It was observed that vigorous stirring greatly increased the rate of HFPE up-take. Immediately after the addition was completed (about two hours reaction time) the product mixture was distilled on a 900-cm. glass-packed column to give the following:

<u>Boiling Range</u>	<u>Weight in Grams</u>	<u>Remarks</u>
56-59°	203	$\begin{array}{c} \text{CF}_3 \quad \text{O} \\   \quad    \\ \text{C}_3\text{F}_7\text{OCF--CF} \end{array}$
59-108°	42	
108-112°	123	$\begin{array}{c} \text{O} \quad \quad \text{CF}_3 \quad \text{O} \\    \quad \quad   \quad    \\ \text{FC}(\text{CF}_2)_4\text{OCF--CF} \end{array} \quad (\text{MEDAF})$
112-155°	87	
155-158°	662	DEDAF
158-172°	22	
Pot Residue	370	Longer chain adducts of HFPE to PFGF.

#### C. Reaction of DEDAF with Methanol

A 1-liter polyethylene bottle was charged with CH<sub>3</sub>OH (200 g., 6.25 moles) and a stirring bar, and was fitted with an addition funnel containing DEDAF (662 g., 1.15 moles). The system was vented to a -183° trap. The alcohol was stirred and the DEDAF was rapidly added dropwise. A small exotherm was observed but no HF collected in the -183° trap. After the addition was completed the mixture was stirred for 16 hours. It was then poured into an excess of water and the bottom layer was separated and dried over molecular sieve to give 599 g. (87% yield) of DEDAME.

Attempted purification by preparative scale GLC gave a low yield of sym-DEDAME of only 92% purity. Infrared spectra of the sym and unsym-DEDAME isomers are shown in Figures 1 and 2.

## II. Synthesis of Perfluorostyrene

### A. Small Scale Reactions of Pentafluorophenyl Iodide with Iodotrifluoro Ethylene

Small scale reactions have been run in both open and closed systems.

#### Open System Reaction

A stirring bar, Fisher purified electrolytic copper dust (19.2 g., 0.30 mole), dimethylacetamide (180 ml.),  $C_6F_5I$  (29.4 g., 0.10 mole), and  $CF_2=CFI$  (20.8 g., 0.10 mole) were placed in a 250-ml. flask fitted with a water-cooled condenser topped by a  $-78^\circ$  condenser vented to a  $-183^\circ$  trap. The reaction mixture was stirred and slowly heated. After 38 minutes the temperature had reached  $65^\circ$  and a slight clouding was observed. The mixture then gradually became a darker red color as the temperature was increased. At a temperature of  $110^\circ$  a slow reflux was observed. After 2 1/2 hours a temperature of  $142^\circ$  was reached and then it began to fall. After another 40 minutes the reaction mixture was at  $135^\circ$  and heating was discontinued. Distillation of the mixture gave a fraction boiling at  $106-108^\circ$  which was shown by GLC (6', 5% Bentone 34 and 5% Diisodecylphthalate on Gas Chrom P,  $30^\circ$ ) to be 95%  $C_6F_5CF=CF_2$ ; an infrared spectrum (Figure 3) was identical to that of an authentic sample of perfluorostyrene. The total yield of 10.2 g. represents a 41% yield.

#### Closed System Reaction

A 3-oz. Fischer-Porter tube was charged with  $C_6F_5I$  (29.4 g., 0.10 mole),  $CF_2CF_2I$  (20.8 g., 0.10 mole), Cu (19.2 g., 0.30 mole), and DMA (19 ml.) and put into a heater-shaker. The temperature was gradually raised to  $98^\circ$  over a 5 1/2 hour period and then maintained at this temperature for one hour. The mixture was then cooled to ambient temperature and the liquid product was analyzed by GLC to determine that  $C_6F_5CF=CF_2$  had been synthesized in approximately 25% yield.

B. Scale-up of Reaction of Pentafluorophenyl  
Iodide with Iodotrifluoroethylene

A stirring bar, Fisher purified electrolytic copper dust (254 g., 4.0 moles), dimethylacetamide (1,500 ml.),  $C_6F_5I$  (500 g., 1.70 moles), and  $CF_2=CFI$  (354 g., 1.70 moles) were placed in a 5-liter flask fitted with a water-cooled condenser topped by a  $-78^\circ$  condenser vented to a  $-183^\circ$  trap. The reaction mixture was stirred and slowly heated to  $\sim 140^\circ$  where it was maintained for 16 hours. An infrared spectrum of the volatiles caught in the  $-183^\circ$  trap (88 g.) indicated the presence of  $CF_2=CF-CF=CF_2$ .

The product mixture was distilled on a glass-packed column to give the following:

<u>Boiling Range</u>	<u>Weight in Grams</u>
31-76°	31
76-108°	121
108-120°	126
120-145°	54

The fractions boiling from  $76^\circ$  to  $120^\circ$  were re-distilled on a spinning band column to give the following:

<u>Boiling Range</u>	<u>Weight in Grams</u>	<u>% <math>C_6F_5CF=CF_2</math> by GLC</u>
56-87°	18	
87-88°	47	
88-92°	38	
92°-120°	14	48
120°	47	99
121-122°	65	99
Pot Residue	7	

The above represents 119 g. of  $C_6F_5CF=CF_2$  (28% yield).

### III. Attempted Syntheses of Perfluorostyrene Epoxide

#### A. Reaction of Benzoyl Fluoride With Hexafluoropropylene Epoxide

A 13-ml. ampoule was charged with  $\text{C}_6\text{F}_5\overset{\text{O}}{\parallel}\text{CF}$  (0.68 g., 3.17 mmoles) and  $\text{CF}_3\overset{\text{O}}{\triangle}\text{CF}_2$  (0.53 g., 3.18 mmoles) and heated at 175° for 48 hours. Examination of the liquid product by GLC and infrared spectra gave no indication of the formation of the desired epoxide.

#### B. Reaction of Perfluorostyrene with Oxygen

A stirring bar was placed in a 1-liter Vycor flask; the flask was then charged with  $\text{C}_6\text{F}_5\text{CF}=\text{CF}_2$  (20.0 g., 80.6 mmoles), cooled in liquid air, evacuated, and connected to a vacuum manifold. A cylinder of  $\text{O}_2$  containing 0.75%  $\text{Cl}_2$  was also connected to the manifold. After the flask warmed to ambient temperature it was opened to the manifold and irradiated with U.V. light from a Hanovia 60-watt table lamp. The pressure of  $\text{O}_2/\text{Cl}_2$  in the manifold and flask was maintained at approximately atmospheric pressure. After 24 hours 62% of the theoretical amount of  $\text{O}_2$  for reaction to the epoxide had been added. After 30 hours the flask was opened and considerable fuming occurred. A colored liquid (8.7 g.) was removed, and a small amount of colored polymeric solid was left. A GLC of the liquid product compared with  $\text{C}_6\text{F}_5\text{CF}=\text{CF}_2$  as a reference indicated no  $\text{C}_6\text{F}_5\text{CF}=\text{CF}_2$  to be present. A crude distillation was carried out. A volatile fraction was obtained and was found to be  $\text{SiF}_4$ . An infrared spectrum (Figure 4) of an intermediate boiling fraction, indicated the presence of both aliphatic and aromatic acid fluoride groups (b. ~100°). A reference infrared spectrum of pentafluorobenzoyl fluoride is shown in Figure 5. An infrared spectrum (Figure 6) of the viscous pot residue did not indicate any  $\text{-CF}\overset{\text{O}}{\parallel}$ .

In an attempt to increase the  $\text{O}_2$ /styrene ratio a second reaction was attempted.

Into a 1-liter Vycor flask connected by a glass "T" to an inverted 5-liter flask was added 10.0 g. (40mM) of  $C_6F_5CF=CF_2$ . The lower flask was cooled to  $-183^\circ$ , evacuated, then warmed to room temperature. Oxygen, containing 0.75% chlorine, was then added to the system to a pressure of 190 mm (approximately 60mM). While stirring with a magnetic stirrer, the styrene in the lower flask was heated to  $100^\circ$  and irradiated with a 40-watt Hanovia model 30620 U. V. lamp. After irradiation for 1.5 hours no detectable change in  $O_2$  pressure was noted, however, the liquid in the Vycor flask changed from the original clear liquid to dark brown. On removal of the overgases (principally  $COF_2$  and  $SiF_4$ , by IR analysis) and the high boiling vacuum transferable liquid ( $C_6F_5COF$  and  $C_6F_5CF=CF_2$ ) a dark viscous residue remained. No evidence was found for the presence of the desired epoxide.

#### C. Reaction of $H_2O_2$ with Perfluorostyrene

To a 250-ml., 3-neck flask fitted with a thermometer, a dropping funnel, and a Vigreux column which was vented to a  $-183^\circ$  cold trap was added 20 ml. of  $H_2O$ , 10.5 g. of KOH and 125 ml. of  $CH_3OH$ . The solution was cooled to  $-40^\circ$ , and while stirring with a magnetic stirrer 60 ml. of 50%  $H_2O_2$  was slowly added. To this reaction mixture, at  $-40^\circ$ , was added dropwise 24.8 g. (0.1 mole) of  $C_6F_5CF=CF_2$ . On completion of addition the mixture was stirred for 2 hours at  $-40^\circ$ , then 16 hours at ambient temperature. The mixture separated into two layers. The lower layer was found to be unreacted styrene, 12.5 g. No other reaction products were detected.

#### IV. U.V. Initiated Polymerization of Perfluorostyrene

Into a 1-liter Vycor flask was placed 5 g. (20mM) perfluorostyrene. The flask was cooled to  $-183^\circ$ , evacuated, then exposed to a 40-watt Hanovia U.V. lamp for 72 hours at ambient temperature. At the end of this time the volatiles were removed at  $100^\circ$  under vacuum leaving a low melting solid polymer. An infrared spectrum of this polymer is

shown in Figure 7. Infrared analysis of the volatiles showed the presence of  $\text{SiF}_4$  and  $\text{CO}_2$  (presumed to be due to air leakage in the system).

V. Synthesis of 1-Iodo-1-Heptafluoro-  
propoxy- 1,2,2,2-tetrafluoroethane

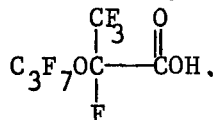
A. Attempted Reaction of Potassium Iodide  
With 2-Heptafluoropropoxy-  
tetrafluoropropanoyl Fluoride

In an attempt to effect the reaction  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{CF} + \text{KI} \longrightarrow \text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{I}$ , a 300 ml. stainless steel autoclave was charged with  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{CF}$  (100 g., 0.30 mole) and KI (60 g., 0.36 mole) and heated at  $200^\circ$  for 8 hours. Only unreacted  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{CF}$  was obtained as a liquid product.

B. Synthesis Using the Hunsdiecker Reaction

1. Synthesis of  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COOH}$

Calcium chloride (90 g., 0.81 mole) was dissolved in 200 g. of  $\text{H}_2\text{O}$ . To this solution  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{CF}$  (120 g., 0.36 mole) was added with stirring. The mixture was stirred for 16 hours and then filtered to remove  $\text{CaF}_2$ . The filtrate was transferred to a separatory funnel where the bottom layer was removed yielding 116 g. (97% yield) of



2. Reaction of  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COOH}$  with  $\text{Ag}_2\text{O}$

Dioxane (100 ml.),  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{COH}$  (20.0 g., 60.2 mmols), and  $\text{Ag}_2\text{O}$  (7.0 g., 30.1 mmols) were stirred together for 48 hours. The

mixture was then filtered and the filtrate was evaporated to dryness to leave 26.5 g. (100% conversion) of white, crystalline  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{COAg}$ .

3. Reaction of  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{COAg}$  with  $\text{I}_2$

Iodine (17.8 g., 70 mmoles) and  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{COAg}$  (26.5 g., 60 mmoles) were mixed together and placed in a 250-ml. flask fitted with a distilling head and condenser emptying into a receiver vented to a  $-183^\circ$  trap. The reaction mixture was heated at  $\sim 175^\circ$  for 16 hours and  $\sim 2$  g. of liquid product was obtained. An infrared spectrum (Fig. 8) of this product is consistent with that expected for  $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{I}$ .

VI. Synthesis of  $\text{p-C}_6\text{F}_4\text{Br}_2$

Into a 1-liter, 2-neck flask fitted with an addition funnel and a reflux condenser connected to a cold trap was placed 455 g. (2.84 moles) of  $\text{Br}_2$ , 5.25 g. (197. mM) of  $\text{AlBr}_3$  and 158 ml. of 30% fuming  $\text{H}_2\text{SO}_4$ . At ambient temperature 105 g. (0.7 mole) of  $\text{p-C}_6\text{F}_4\text{H}_2$  was added dropwise. While stirring with a magnetic stirrer, the mixture was heated to  $60^\circ$  for 3 hours. The mixture was then poured over ice and the lower, dark brown layer, decanted. When this liquid was washed with  $\text{Na}_2\text{CO}_3$  solution a light brown solid was obtained. Washing with sodium bisulfite solution followed by a water wash and drying yielded 127 g. (0.41 mole), 58.5% yield, of  $\text{p-C}_6\text{F}_4\text{Br}_2$ , m.p.  $78-9^\circ$ . An infrared spectrum of this compound is shown in Figure 9.

VII. Synthesis of  $\text{p-BrC}_6\text{F}_4\text{COC}_2\text{F}_5$

Into a 1-liter, 3-neck flask fitted with a thermometer, reflux condenser vented through a  $-183^\circ$  trap and a dropping funnel was added 500 g. (0.162 mole)  $\text{p-C}_6\text{F}_5\text{Br}_2$  and 417 ml. of tetrahydrofuran. The reaction mixture was cooled to  $0^\circ$  and while stirring with a magnetic stirrer 74 ml. (0.162 mole) of  $\text{C}_2\text{H}_5\text{MgBr}$  in ether was added dropwise.

After addition, mixing was continued for 2 hours at 0°, then 15.8 g. (0.162 mole) of CuCl<sub>2</sub> was added. The ice-water bath was removed and the mixture was stirred for an additional 2 hours. To this mixture was then added 69.5 g. (0.162 mole) of C<sub>7</sub>F<sub>15</sub>COCl and mixing was continued for 16 hours.

The reaction mixture was again cooled to 0° and 6N HCl added. After removal of the solids by filtration, the aqueous layer was decanted and distillation of the organic layer through an 18", glass helices packed, distillation column yielded 53.4 g. (0.0854 mole) of p-BrC<sub>6</sub>F<sub>4</sub>COC<sub>7</sub>F<sub>15</sub>, a low melting solid, b.p. 99°/2mm. This represents a 53% yield. An infrared spectrum of this compound is shown in Fig. 10. Preliminary NMR analysis is consistent with the structure assigned this compound.

FLUORINE NMR SPECTRAL DATA FOR  
p-BrC<sub>6</sub>F<sub>4</sub>COC<sub>7</sub>F<sub>15</sub>

<u>Desig.</u>	<u>Chemical Shift (Subst. CF<sub>3</sub>COOH)</u>	<u>Pattern &amp; Splitting</u>	<u>Rel. Area</u>	<u>Assignment</u>
A	-6ppm	Multiplet	0.6	impurity
B	+2.7	Triplet	2.8	CF <sub>3</sub>
C	+35	-	0.3	impurity
D <sub>1</sub>	+40	Broad	2.1	CF <sub>2</sub> next to CO
D <sub>2</sub>	+43	Broad	8.5	CF <sub>2</sub>
D <sub>3</sub>	+47.9	Broad	1.9	CF <sub>2</sub> next to CF <sub>3</sub>
D <sub>4</sub>	+51.4	Multiplet	1.9	2CF on ring
E	+59.3	Broad	1.9	2CF on ring

The impurities noted are typical of compounds containing a C<sub>8</sub> fluorocarbon chain derived from 3M's perfluorooctanoic acid.



# VIII. Synthesis of p-BrC<sub>6</sub>F<sub>4</sub>C<sub>8</sub>F<sub>17</sub>

## 1. AlF<sub>3</sub> Catalyzed SF<sub>4</sub> Reaction

Into a 1.4-liter stainless steel high pressure reactor was placed 49.0 g. (0.078 mole) of p-BrC<sub>6</sub>F<sub>4</sub>COC<sub>7</sub>F<sub>15</sub>, 6.0 g. (0.07 mole) of AlF<sub>3</sub> and 78.0 g. (0.722 mole) of SF<sub>4</sub>. The mixture was heated and rocked for 120 hours at 170°. The reactor was cooled and vented and the reaction mixture was washed with a NaHCO<sub>3</sub> solution followed by a water wash. Distillation through a glass helices packed column gave 43 g. of the starting ketone (p-BrC<sub>6</sub>F<sub>4</sub>COC<sub>7</sub>F<sub>15</sub>).

## 2. SF<sub>4</sub> Reaction in HF

The recovered ketone from the previous reaction, 43 g. (0.069 moles), 20 ml. anhydrous HF, and 27 g. (0.25 mole) of SF<sub>4</sub> were added to a 300-ml. stainless steel high pressure reactor. The mixture was heated and rocked for 16 hours at 180°. The reactor was cooled, vented, and the solid reaction product was dissolved in Et<sub>2</sub>O, then washed with NaHCO<sub>3</sub> and with H<sub>2</sub>O. The Et<sub>2</sub>O was removed under vacuum leaving a brown solid. Recrystallization from EtOH gave 33.8 g. (0.052 mole), 76% yield, of p-BrC<sub>6</sub>F<sub>4</sub>C<sub>8</sub>F<sub>17</sub>, m.p. 53.1° by DSC. An infrared spectrum of this compound is shown in Figure 11.

# IX. Hydrolysis of DEDAF

To a 500-ml. polyethylene bottle containing a stirring bar and 250 ml. of H<sub>2</sub>O was added 300 g. (0.251 mole) of mixed DEDAF isomers (by GLC, 70% sym and 30% unsym DEDAF). The DEDAF was added dropwise and the solution stirred overnight. CaCl<sub>2</sub> solution was added and the precipitated CaF<sub>2</sub> removed by filtration. The reaction mixture separated into two phases. The lower layer was decanted and distilled through an 18" distillation column packed with 3/16" glass helices yielding 174.2 g. of DEDA isomers boiling at 148°/1.5mm. Neutralization equivalent calculated for C<sub>11</sub>F<sub>20</sub>H<sub>2</sub>O<sub>6</sub>, 286. Found, 283, 286. An infrared spectrum of these mixed isomeric acids is shown in Fig. 12.

# X. Synthesis of DEDN

Using the method shown in IC, 382 g. (0.663 mole) of DEDAF (as

above 70% sym and 30% unsym.) was converted to the dimethyl ester by reaction with methanol.

The diester was washed, dried over molecular sieve, then placed in a 2-liter, 3-neck flask fitted with a stirrer, a gas inlet tube, and a reflux condenser connected to a bubble counter and a  $-183^{\circ}$  trap. To the diester was added 500 ml. of  $\text{Et}_2\text{O}$ . The solution was cooled to  $0^{\circ}$  and  $\text{NH}_3$  added at such a rate that only occasional gas passed through the bubble counter. The solution was saturated with ammonia, as noted by an increase in bubble rate in the bubble counter. The  $\text{Et}_2\text{O}$  was removed under vacuum leaving a crystalline white diamide, DEDAA.

The DEDAA was mixed with a large excess of  $\text{P}_2\text{O}_5$  in a 1-liter, 1-neck flask. The solid mixture was heated to  $200^{\circ}$  under vacuum and the volatile product collected as a white solid at  $-78^{\circ}$ . Distillation through an 18" column packed with 3/16" glass helices gave 178 g. (0.354 mole) of the dinitrile, DEDN, b.p.  $151^{\circ}$ . This represents an overall yield of DEDN from DEDAF of 54%. An infrared spectrum of this compound is shown in Figure 13.

#### XI. Pyrolysis of $\text{CF}_3\text{CFCF}_2\text{O}$

A 17-ml. heavy wall Pyrex glass ampoule was evacuated, then charged with a 2.7 g. (16.0 mM) of  $\text{CF}_3\text{CFCF}_2\text{O}$ . The ampoule was heated to  $200^{\circ}$  for 72 hours. After this time it was noted that the walls of the ampoule were coated with a white solid. After cooling for a few minutes the ampoule was placed against a concrete wall. The ampoule received a slight jar and it exploded.

#### XII. Synthesis of HFPE

A 50-l. flask was fitted with an internal cooling coil (connected through a pump to a reservoir of trichloroethylene cooled to  $-78^{\circ}$ ), stirrer, thermometer, addition funnel, and a low-temperature reflux condenser. The flask was charged with methanol (16 l.), water (2.4 l.) and potassium

hydroxide (1,340 g., 23.9 m.) and immersed in a cooling bath of trichloroethylene. The reflux condenser was filled with dry ice and trichloroethylene and dry ice was added intermittently to the cooling bath at a rate such that the temperature of the flask contents maintained at  $-40$  to  $-50^{\circ}$ . While stirring vigorously  $\text{H}_2\text{O}_2$  (8 l.,  $\sim 137$  m.) was added slowly through the addition funnel. As soon as the  $\text{H}_2\text{O}_2$  addition was completed the temperature of the reaction mixture was adjusted to  $-42$  to  $-45^{\circ}$ , and hexafluoropropylene (1,618 g., 10.8 m.) was added by inverting a flask containing the material at  $-78^{\circ}$  and letting the liquid flow through a polyethylene tube which was temporarily inserted beneath the surface of the reaction mixture. The mixture was allowed to warm to  $-38^{\circ}$ , and a vigorous reaction began. Maximum cooling, using both the external bath and internal coil, was required for approximately 10 minutes. Internal cooling was discontinued as the temperature of the reaction mixture began dropping, and the external cooling bath was used to lower the temperature to  $-50^{\circ}$ . At this point the reflux condenser was replaced with a large-bore gas vent which led to a series of traps cooled to  $-78^{\circ}$ . The product mixture was warmed, and at a temperature of  $-30$  to  $-15^{\circ}$  the gaseous product was vigorously evolved.

The crude product was found to be a mixture of the desired hexafluoropropylene epoxide, unreacted hexafluoropropylene, and carbon dioxide. The mixture was bubbled through a 24 inch column containing glass helices and bromine, and then passed through two  $-10^{\circ}$  condensers. (Most of the bromine and 1,2-dibromohexafluoropropane was collected in these traps.) The  $\text{HFPO}/\text{CO}_2$  was then vented to a flask fitted with a  $-78^{\circ}$  condenser where the hexafluoropropylene epoxide was refluxed to remove carbon dioxide. The purified product was then transferred to a cylinder and found to weigh 582 g. (32.5% conversion). GLC analysis indicated essentially pure HFPE containing only a trace of  $\text{CO}_2$ .

### XIII. Synthesis of $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{COF}$

Four reactions were carried out in the synthesis of this acid fluoride. In the first reaction no coolant was used and the temperature

of the reaction rose to about 55°. This resulted in yielding oligomers containing 2, 3 and 4 epoxide units. In the second oligomerization the temperature of the reaction flask was maintained at ~15° by external cooling and the major product obtained was the acid fluoride containing 5 epoxide units; however, a considerable amount of lower oligomers was also obtained. In a third reaction the temperature of the flask was maintained at ~-15°. No reaction occurred at this temperature.

The conditions employed in the fourth reaction appear to be best suited for the synthesis of the desired acid fluoride. This reaction is described below.

Cesium fluoride (10 g., 0.066 moles) and a stirring bar were put into a 5-l. flask and heated at 180° under vacuum for one hour. The flask was then charged with the dimer, trimer, and tetramer acid fluorides from the previous reactions in which 1,491 g. (8.98 moles) of hexafluoropropylene epoxide had been used; to this was added 50 ml. of Diglyme. The flask was connected to a vacuum manifold and degassed. It was then cooled to ~2° and hexafluoropropylene epoxide (1,962 g., 11.8 moles) was added at 1000 mm absolute pressure while vigorous stirring was maintained. The temperature of the reaction mixture was held at 0-4°.

Distillation of the product mixture gave none of the dimer or trimer acid fluoride and only 45 g. (b.p. = 160°) the tetramer. The major product was the pentamer acid fluoride, b.p. = 202°, which weighed 1,349 g. An infrared spectrum of the pentamer acid fluoride is shown in Figure 14. This represents a 39% conversion of the  $\text{CF}_3\text{CFCF}_2\text{O}$  to the desired acid fluoride. Also obtained was 818 g. (24% conversion) of the hexamer acid fluoride, b.p. = 231-5°, and 287 g. of higher boiling oligomers.

XIV. Synthesis of  $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{CONH}_2$  and  $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{CN}$

A 5-liter, 2-neck flask was charged with dry ethyl ether (2,000 ml.) and pentamer acid fluoride (1,188 g., 1.43 moles). A

stirring bar was added, and the flask was fitted with a gas outlet vented through a bubble counter and a gas inlet, exhausting beneath the surface of the liquid. Anhydrous  $\text{NH}_3$  (100 g., 5.88 moles) was bubbled in at a rate such that only occasional bubbles were noted to exit through the bubble counter. After a marked increase in the rate of  $\text{NH}_3$  escaping was observed the addition was continued for an additional 30 minutes. The solution was stirred for 16 hours. Excess  $\text{NH}_3$  and  $(\text{C}_2\text{H}_5)_2\text{O}$  were removed under vacuum, yielding a viscous liquid product.

The pentamer acid amide was transferred to a 2-l., 1-neck flask and mixed with  $\text{P}_2\text{O}_5$  (1,100 g., 7.75 moles). The flask was fitted with a short Vigreux column and distilling head. Heating under full vacuum gave a yellow liquid product. This material was redistilled at atmospheric pressure yielding 944 g. (82% yield) of the pentamer nitrile, b.p. =  $215^\circ$ . An infrared spectrum of this compound is shown in Figure 15.

XV. Synthesis of  $[\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{CN}]_3$  s-Triazine Fluid

The pentamer nitrile (944 g., 1.17 moles) and a stirring bar were placed in a 1-liter, 2-neck flask fitted with a  $-78^\circ$  reflux condenser vented to a  $-183^\circ$  trap and a gas inlet opening above the surface of the liquid. The gas inlet was connected to a cylinder of ammonia, and this material was added as a gas. As the  $\text{NH}_3$  condensed on the reflux condenser and dropped into the nitrile the reaction with this material was extremely vigorous. However, no temperature rise was observed. A total of 70 g. (4.1 moles) of  $\text{NH}_3$  was added. The excess  $\text{NH}_3$  was vented and an infrared spectrum of the product mixture (Fig. 16) indicated that it was a mixture of an amidine and imidoyl amidine. The CN absorption had disappeared.

The  $-78^\circ$  condenser was replaced with a water cooled condenser and the mixture was heated at  $220^\circ$  under reduced pressure (180 mm) for 72 hours. The product mixture was distilled to give 65 g. of lower boilers and 827 g. (94% yield) of a pale yellow liquid, b.p. =  $197^\circ/1.5$  mm. An infrared spectrum of the resultant s-triazine fluid is shown in Figure 17.

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## ILLUSTRATIONS

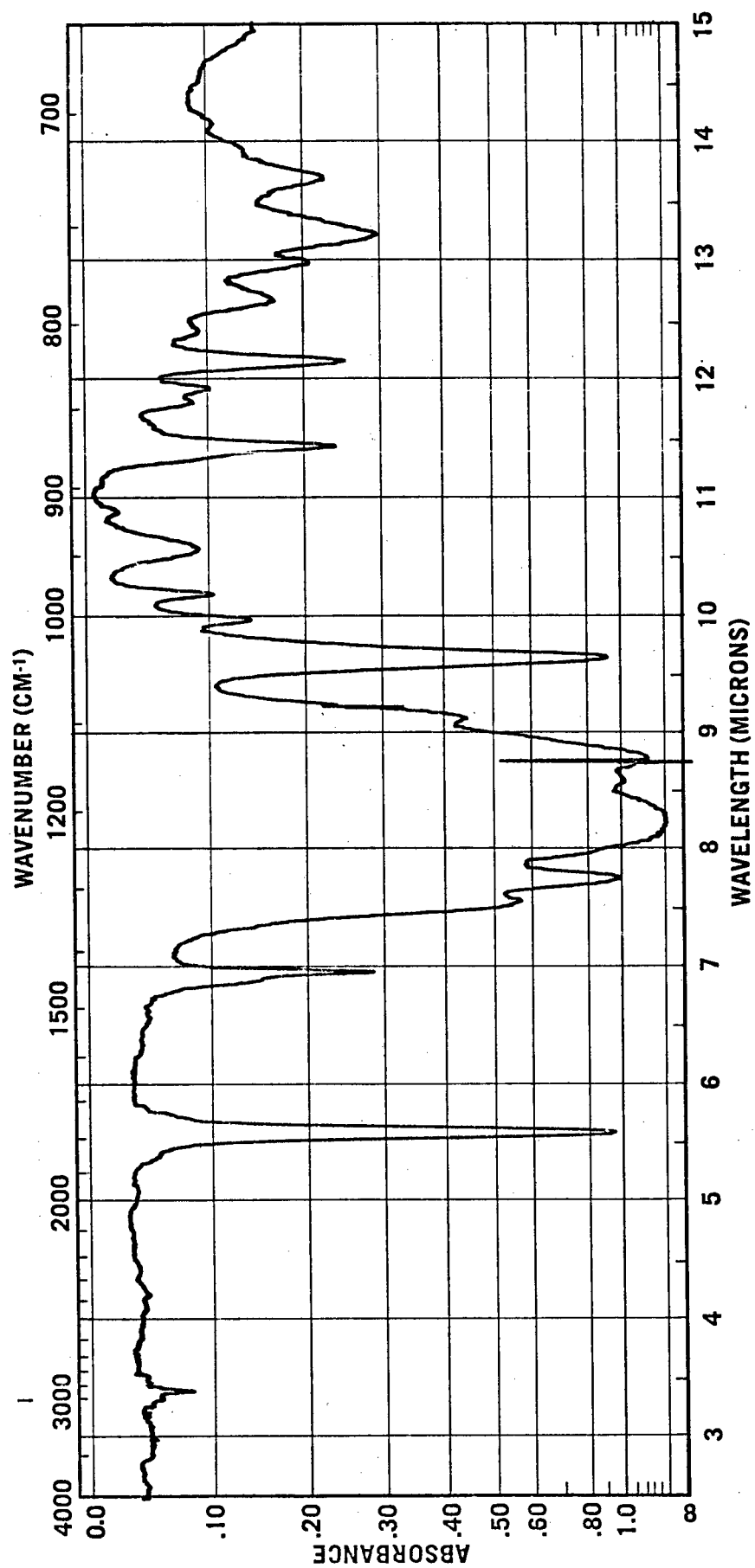


Figure 1

Infrared Spectrum of sym-DEDAME,  $\text{CH}_3\text{OCOCF}(\text{CF}_3)\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)\text{COOCH}_3$   
(liquid)



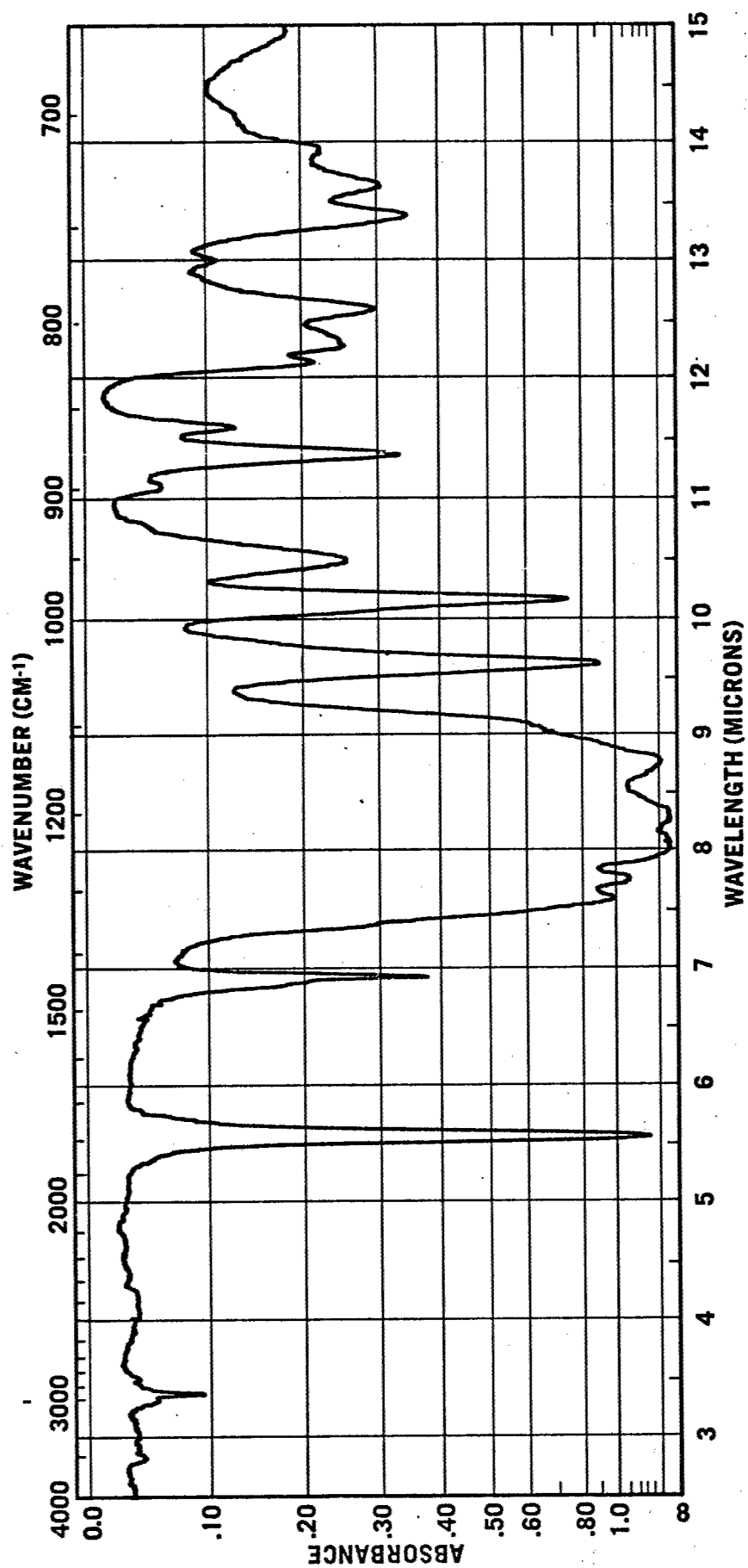


Figure 2

Infrared Spectrum of unsym-DEDAME,  $\text{CH}_3\text{OCO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{COOCH}_3$   
(liquid)

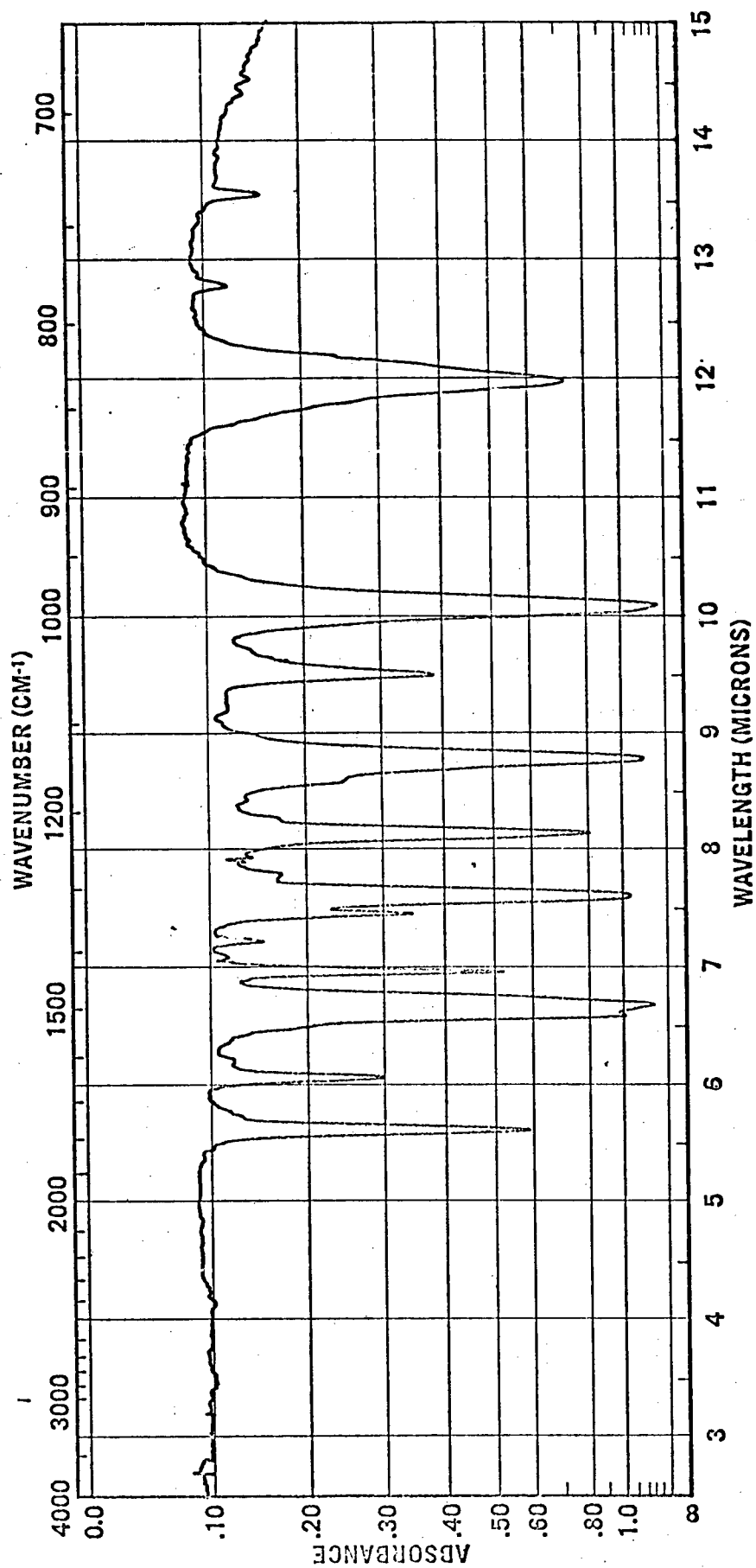


Figure 3  
Infrared Spectrum of  $C_6F_5CF=CF_2$   
(liquid)

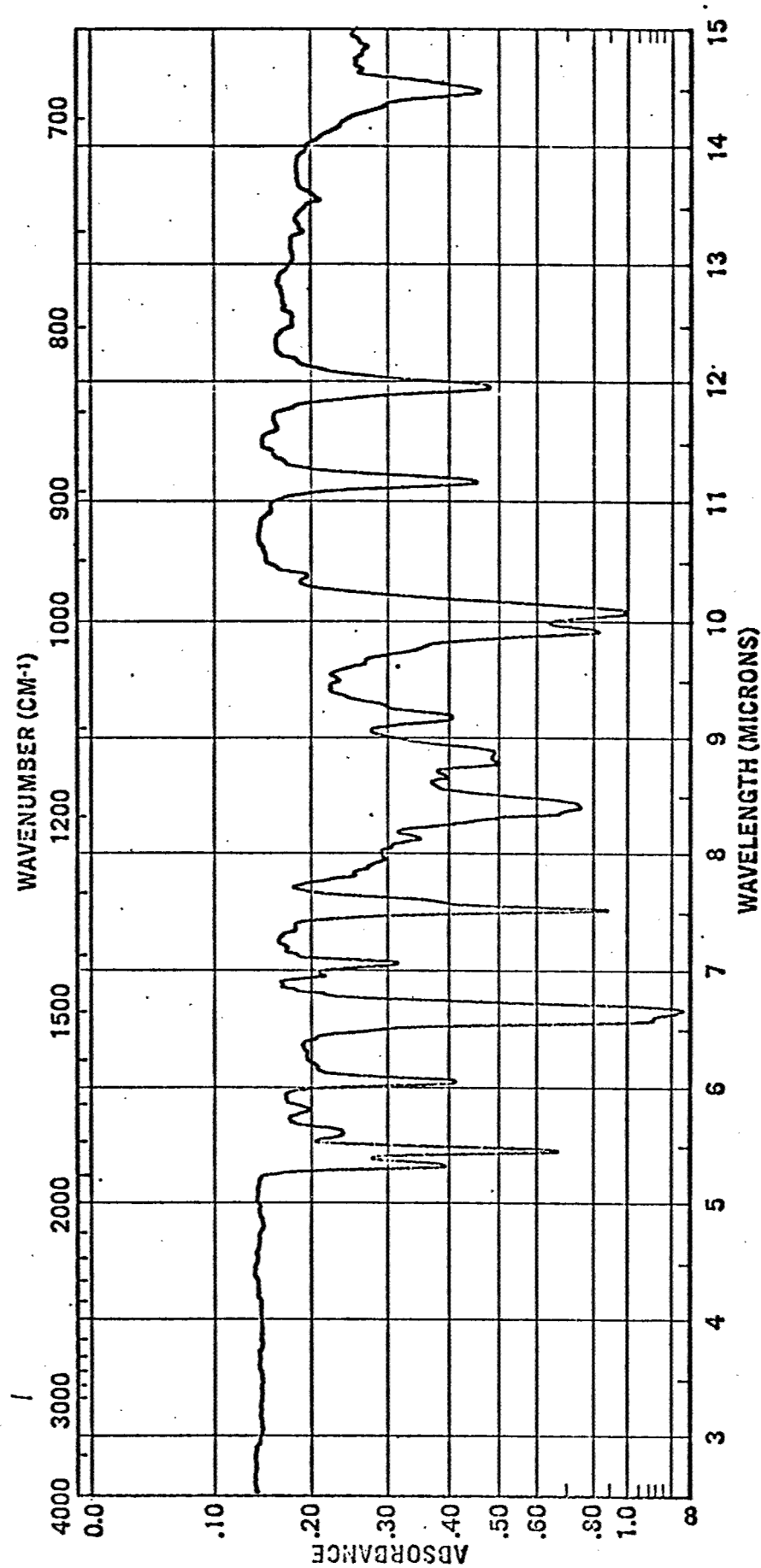


Figure 4

Infrared Spectrum of Crude Product Obtained from  $C_6F_5CF=CF_2/O_2$  Reaction  
(liquid, b.  $\sim 100^\circ$ )

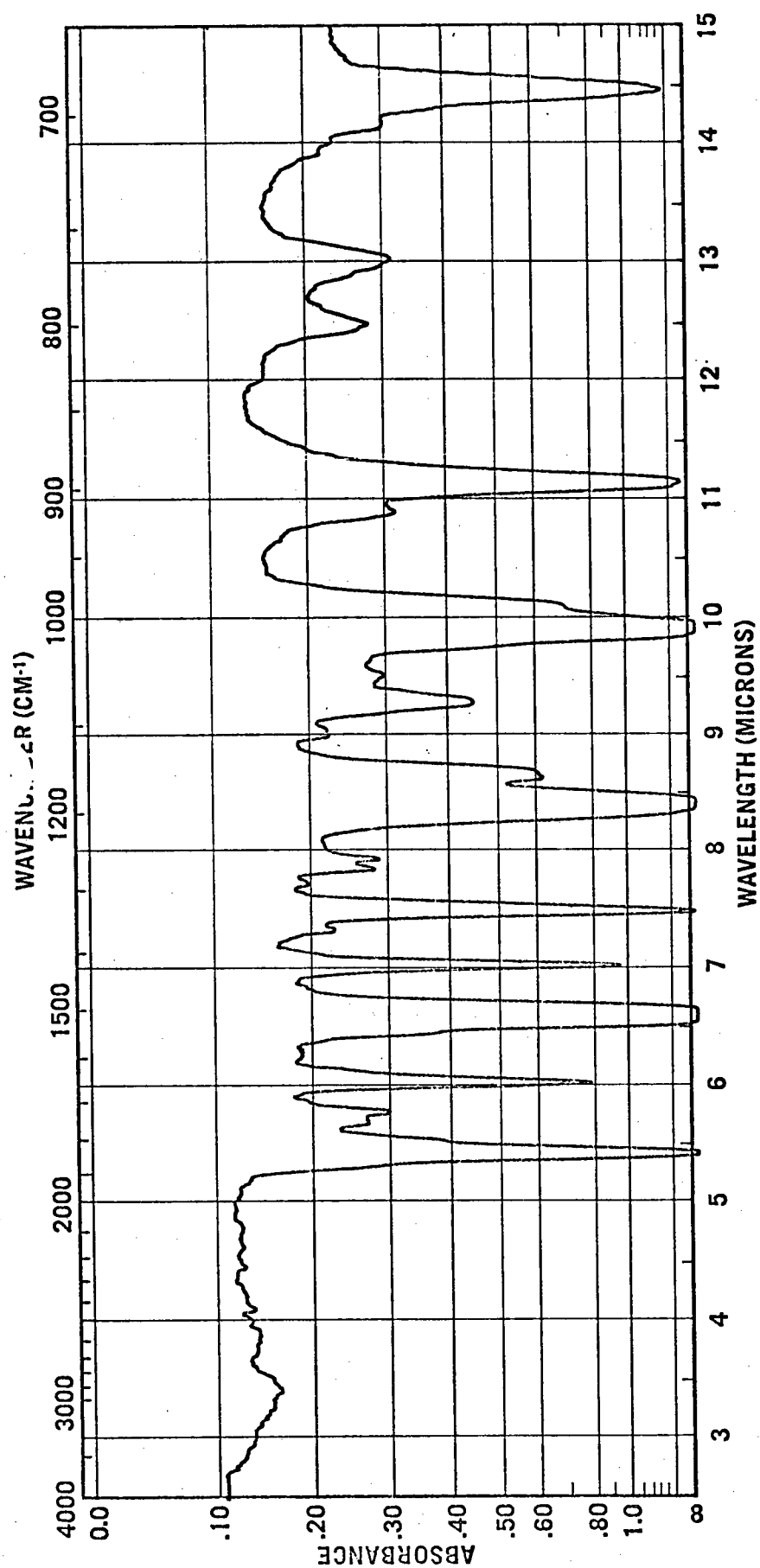


Figure 5  
Infrared Spectrum of Pentafluorobenzoyl Fluoride  
(liquid)

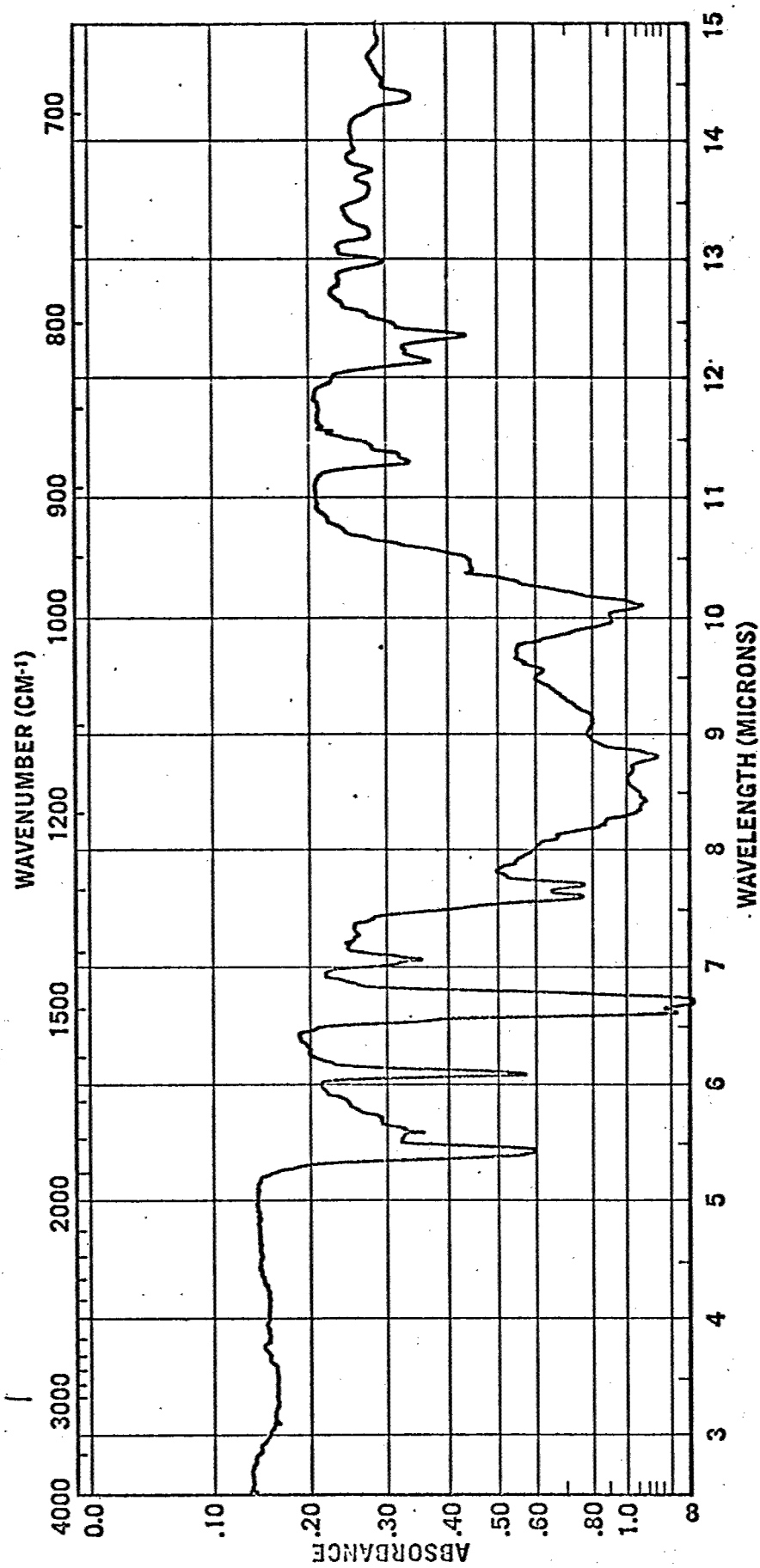


Figure 6  
Infrared Spectrum of Pot Residue from  $C_6F_5CF=CF_2/O_2$  Reaction  
(liquid)

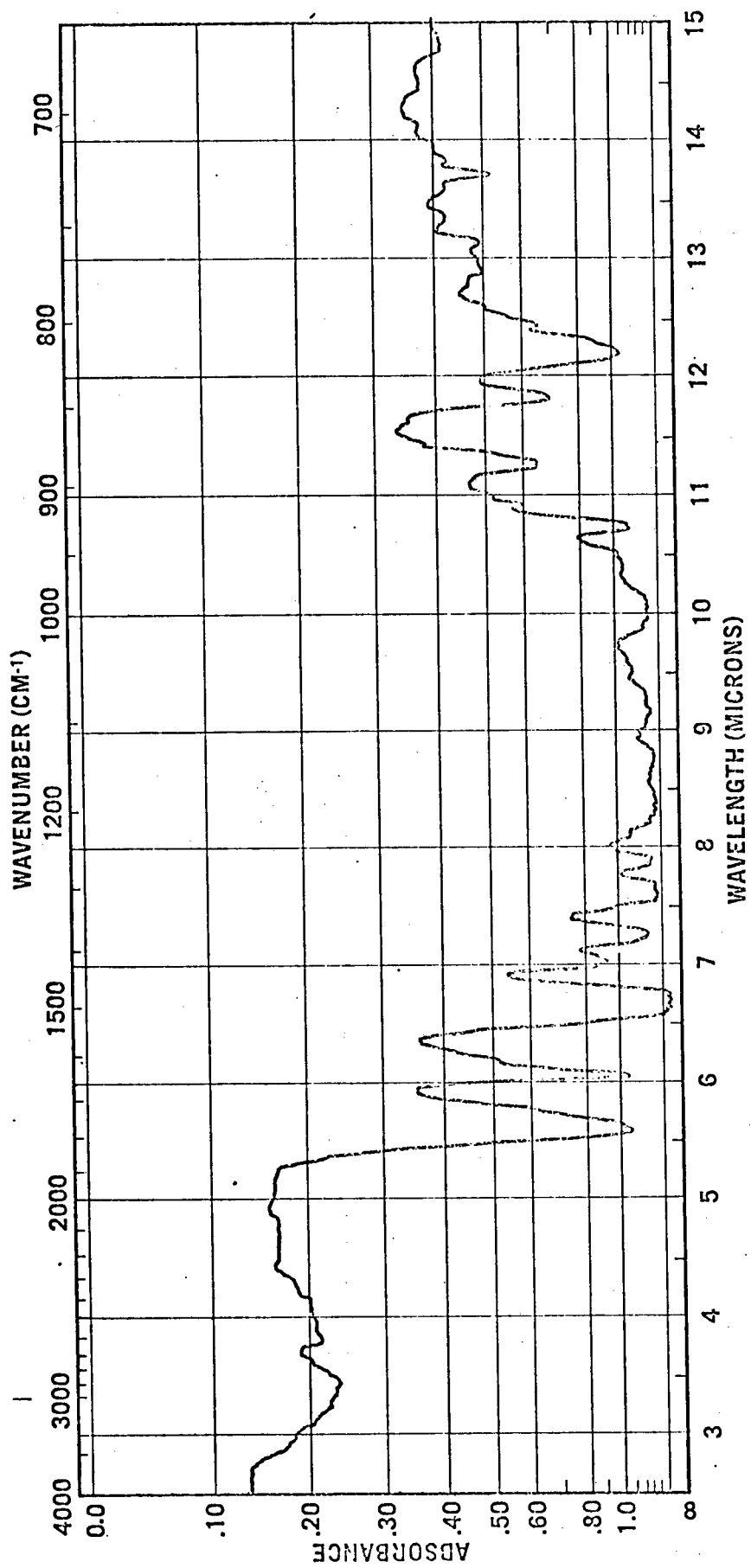


Figure 7. Infrared Spectrum of Poly(perfluorostyrene)

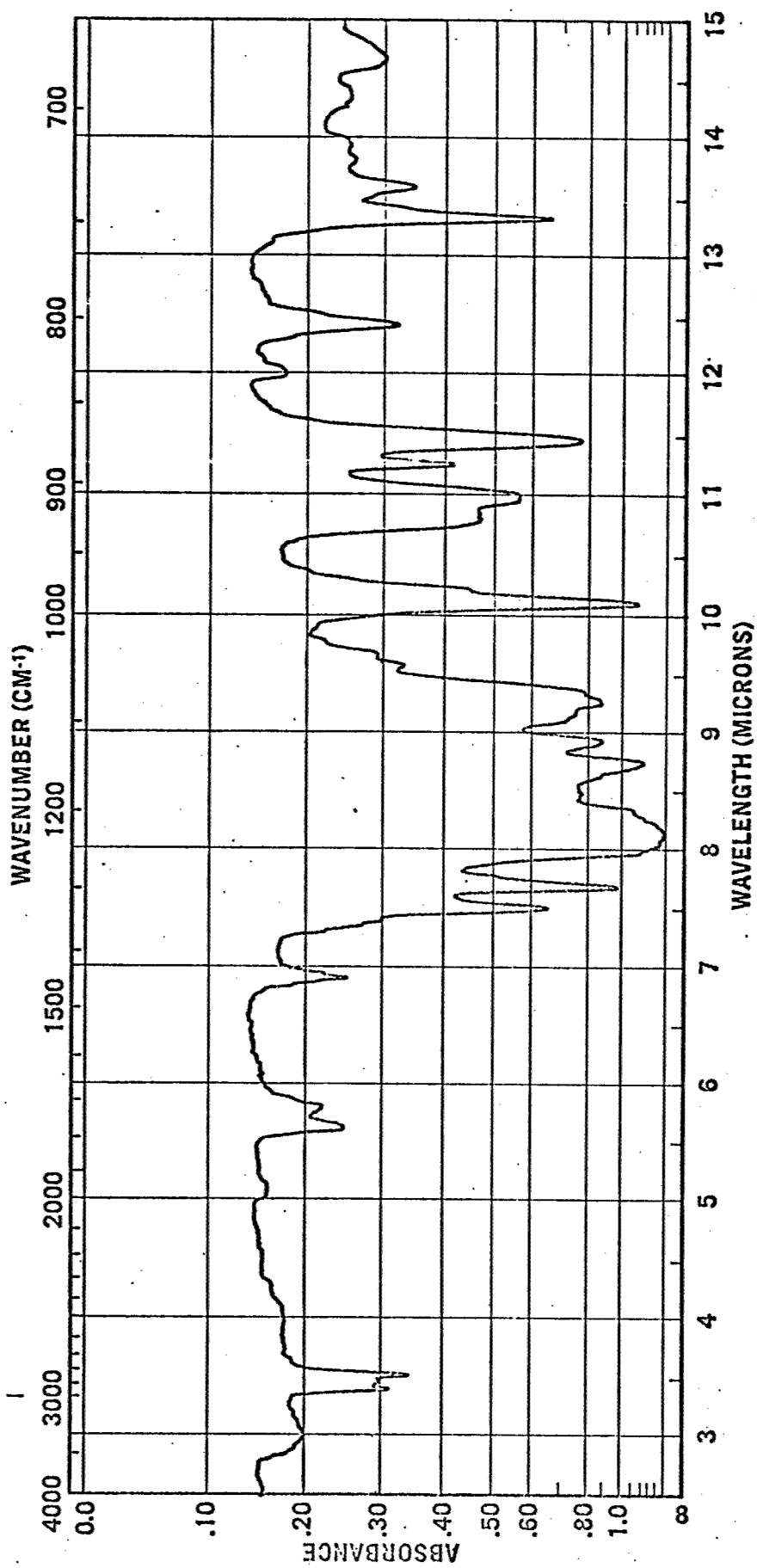


Figure 8

Infrared Spectrum of  $C_3F_7OCF(CF_3)I$   
(liquid, containing some dioxane)

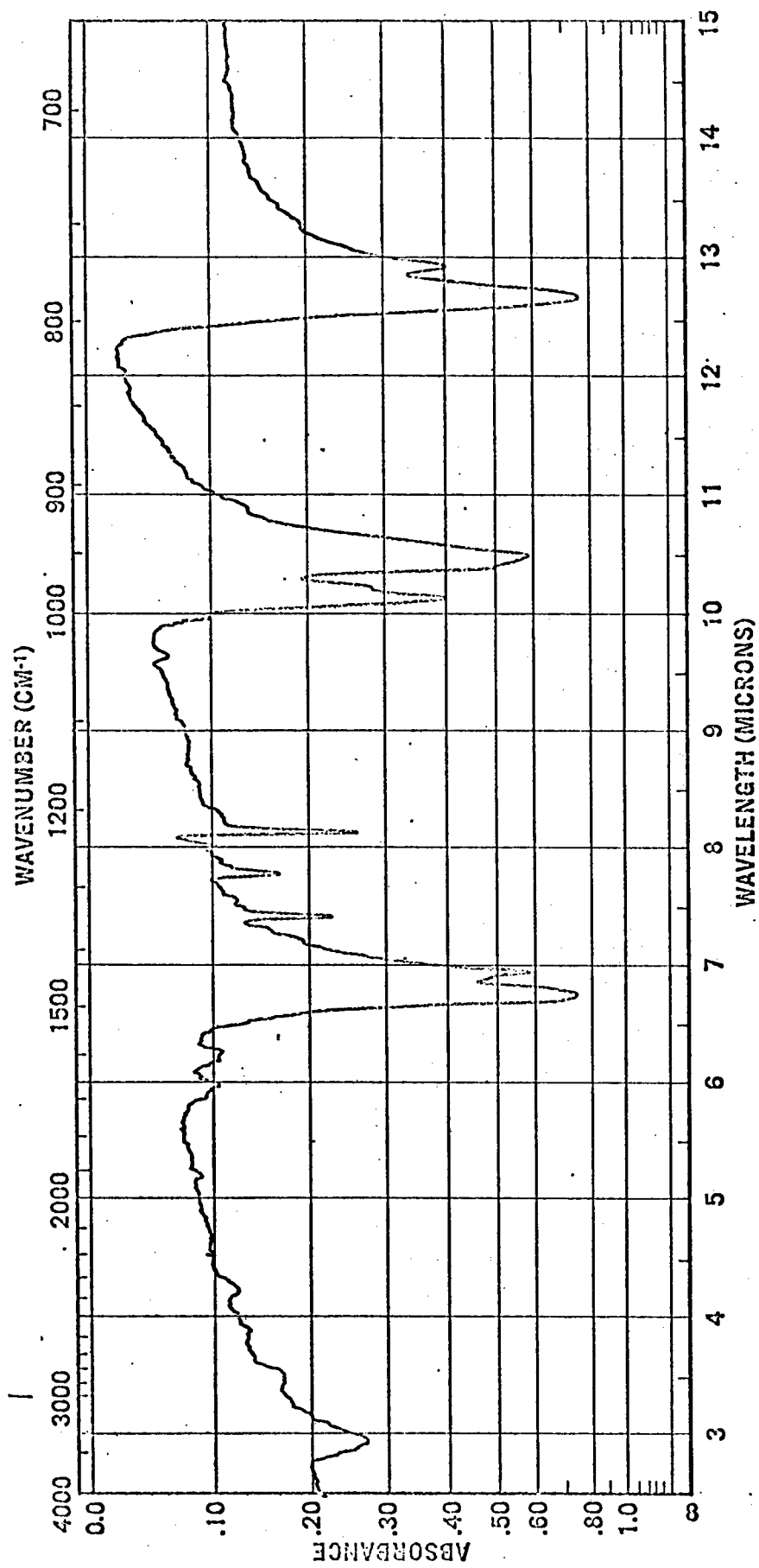


Figure 9. Infrared Spectrum of p-C<sub>6</sub>F<sub>4</sub>Br<sub>2</sub>



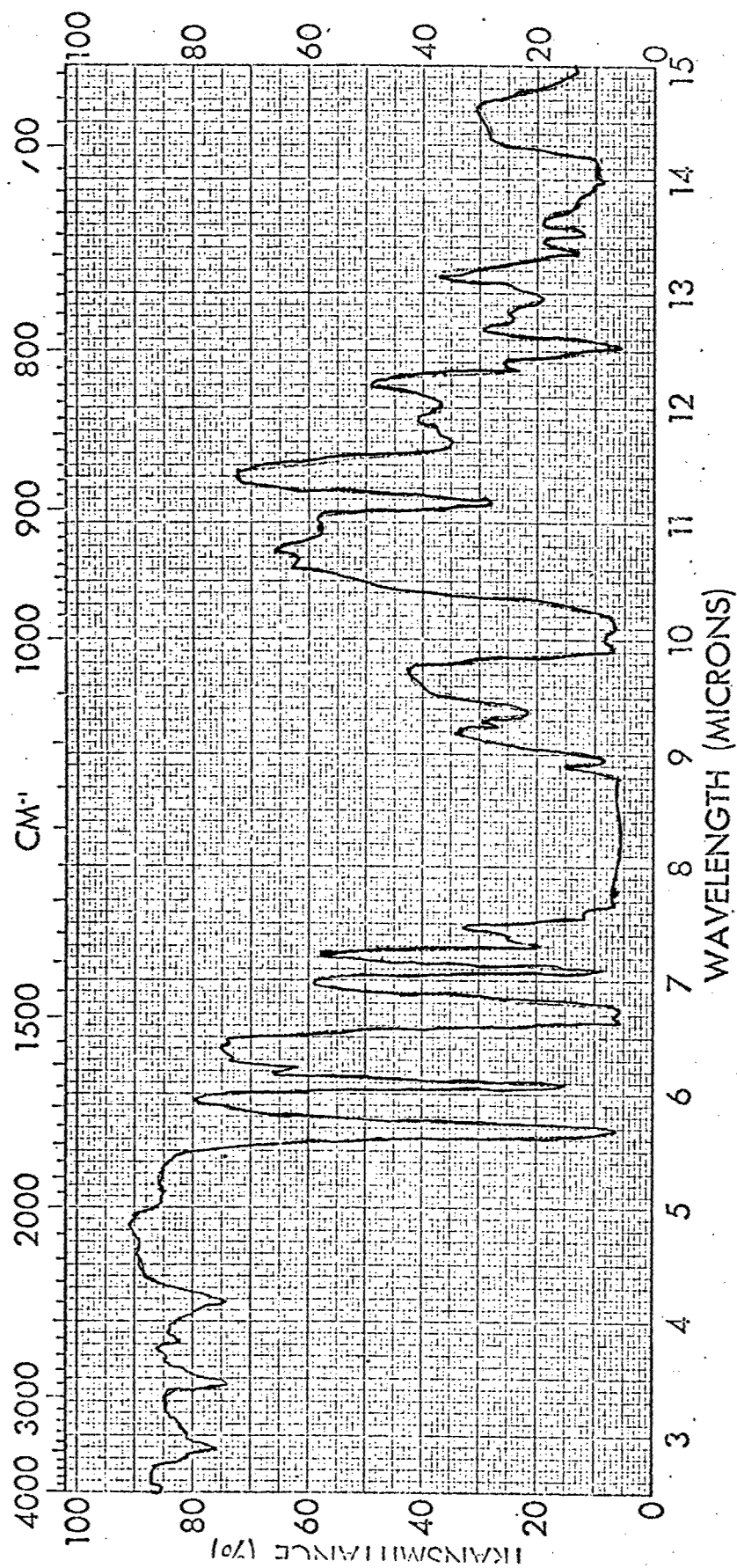


Figure 10. Infrared Spectrum of  $p\text{-BrC}_6\text{F}_4\text{COC}_7\text{F}_{11}$

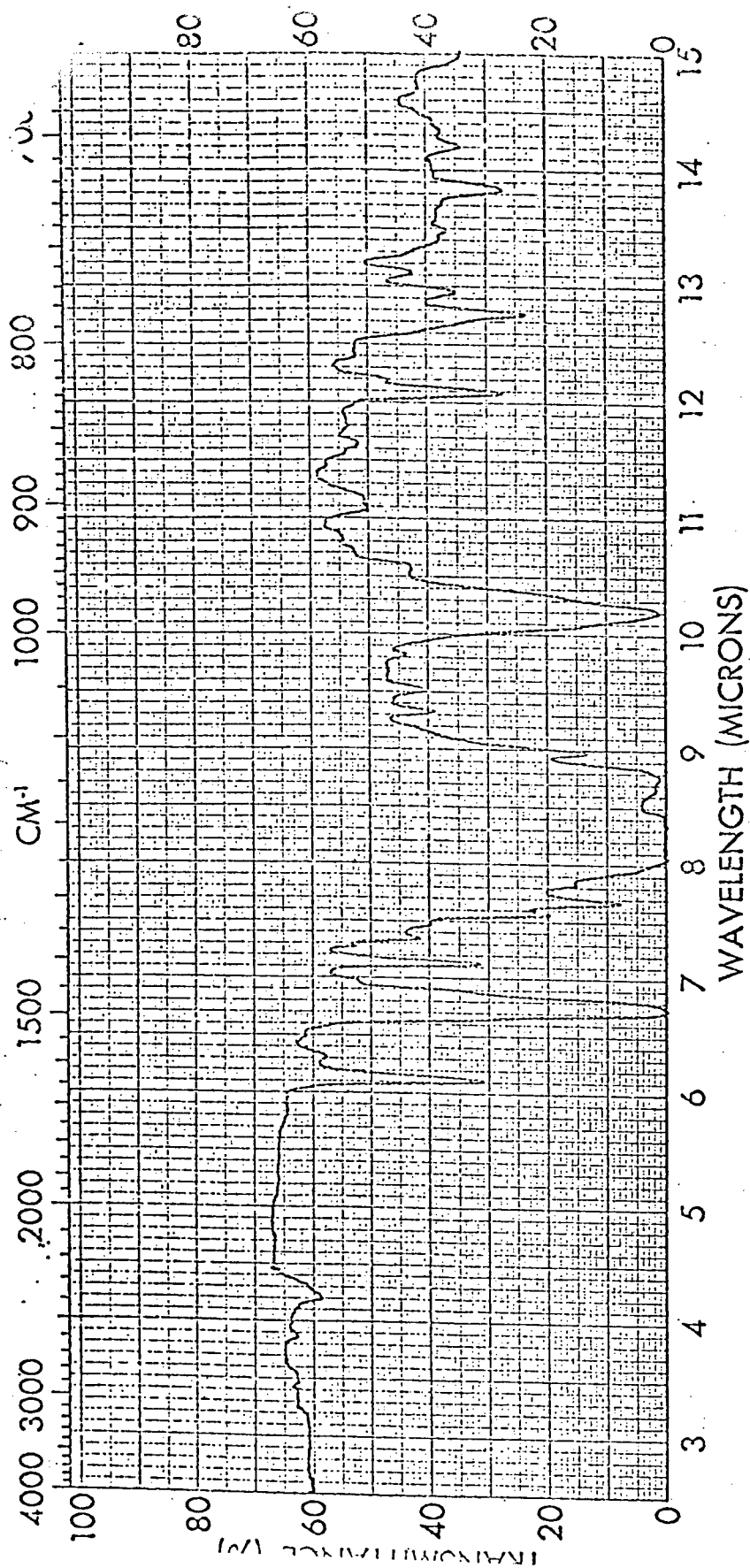


Figure 11.

Infrared Spectrum of  $p\text{-BrC}_6\text{F}_4\text{CF}_3$

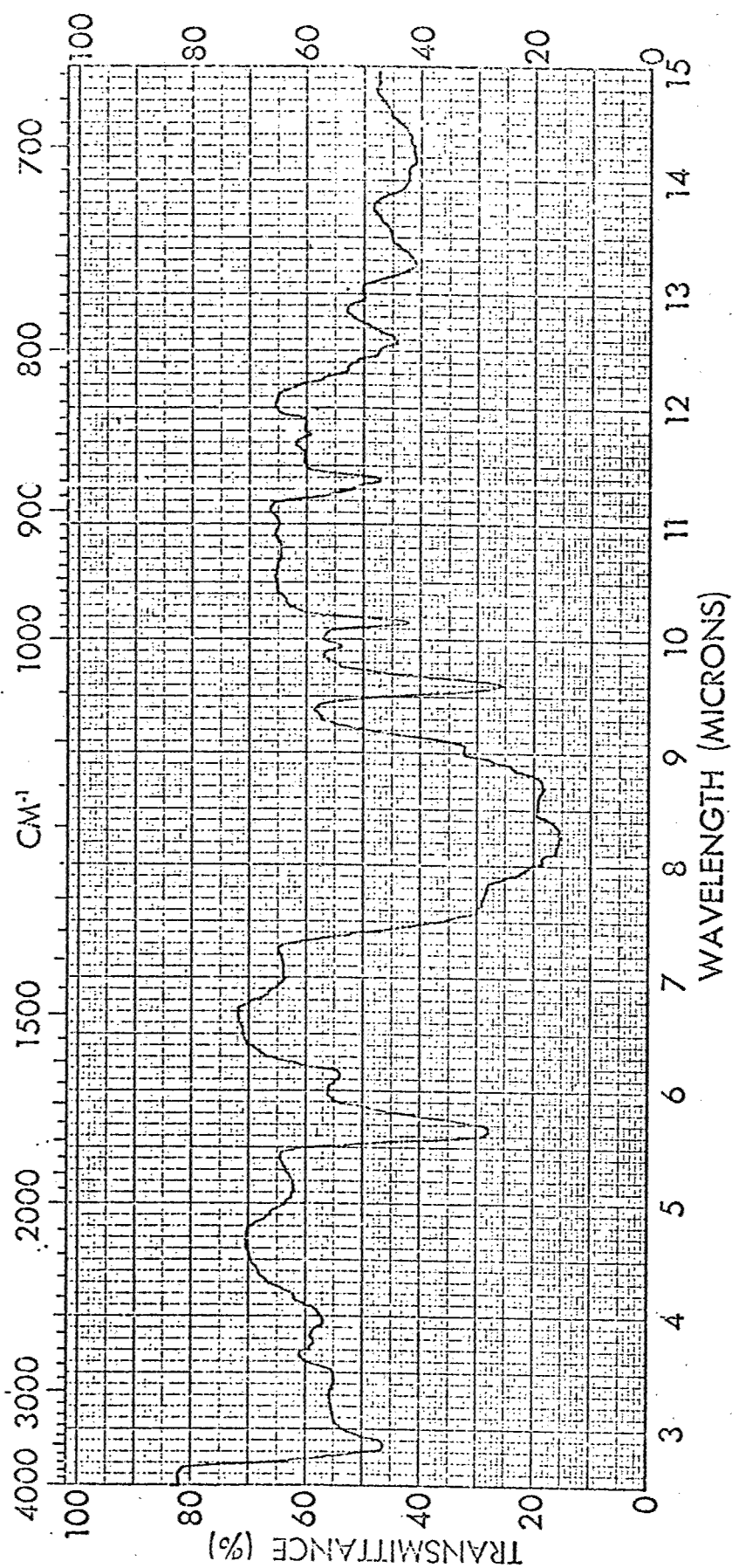


Figure 12. Infrared Spectrum of Mixed DEDA Isomers

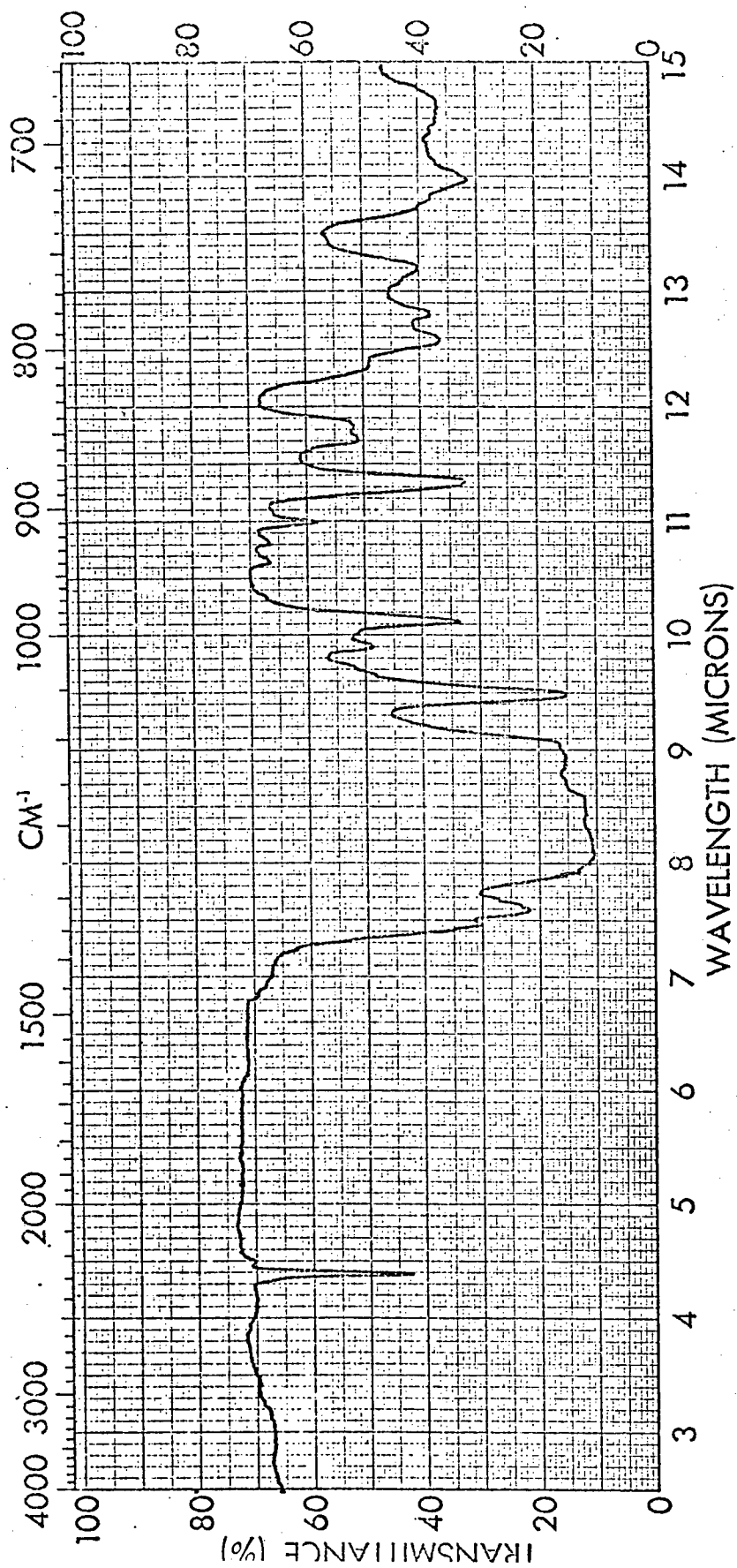


Figure 13. Infrared Spectrum of Mixed DEDN Isomers

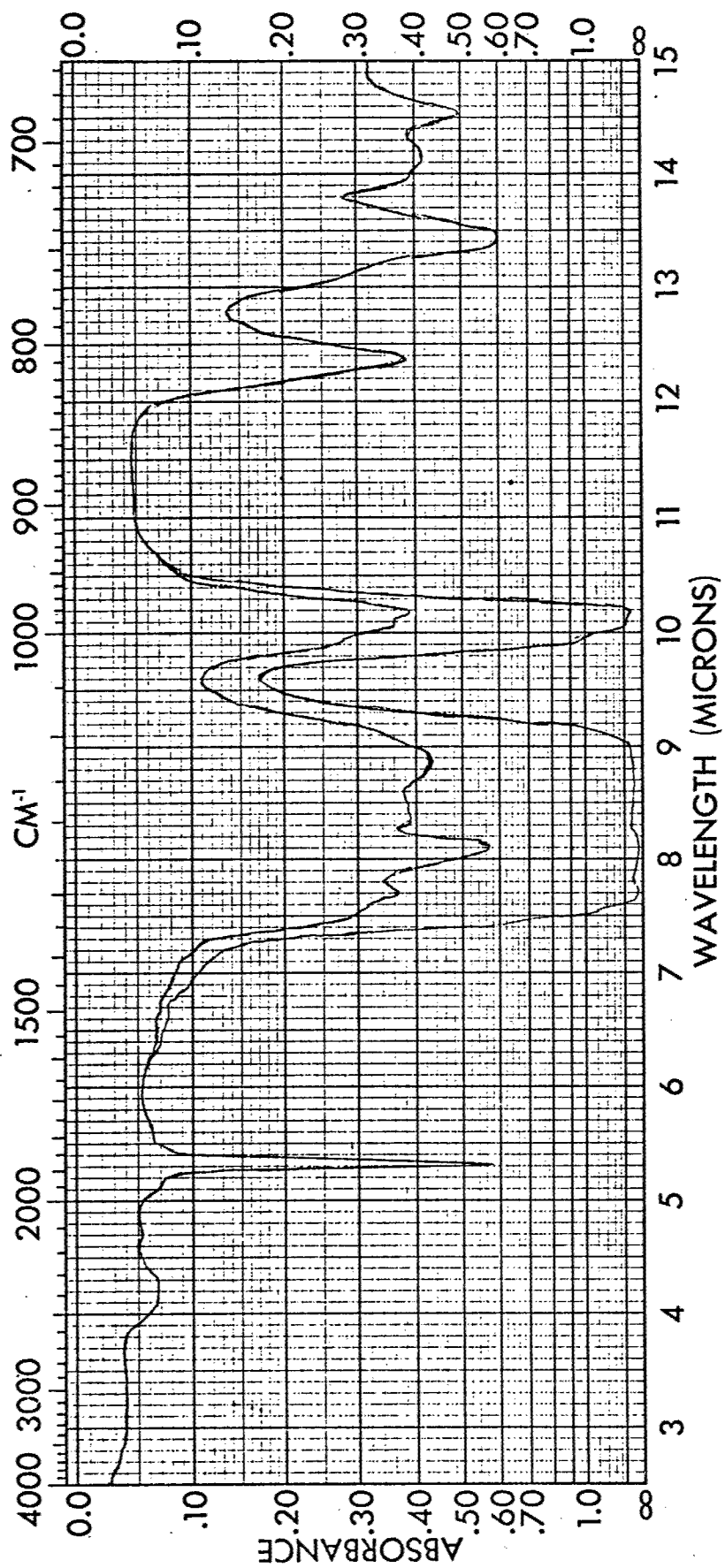


Figure 14

An Infrared Spectrum of  
 $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{COF}$  (liquid)

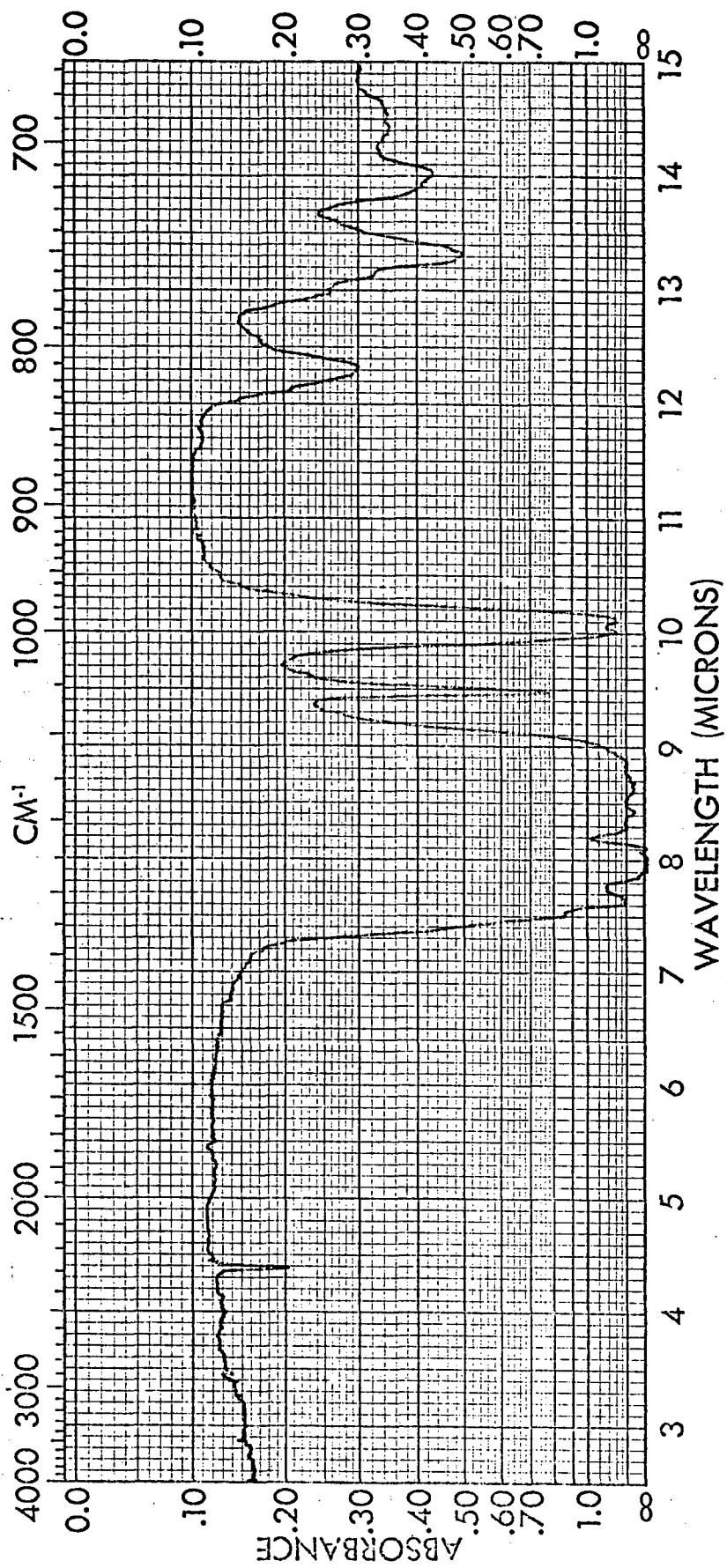


Figure 15.

An Infrared Spectrum of  
 $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{CN}$  (liquid)

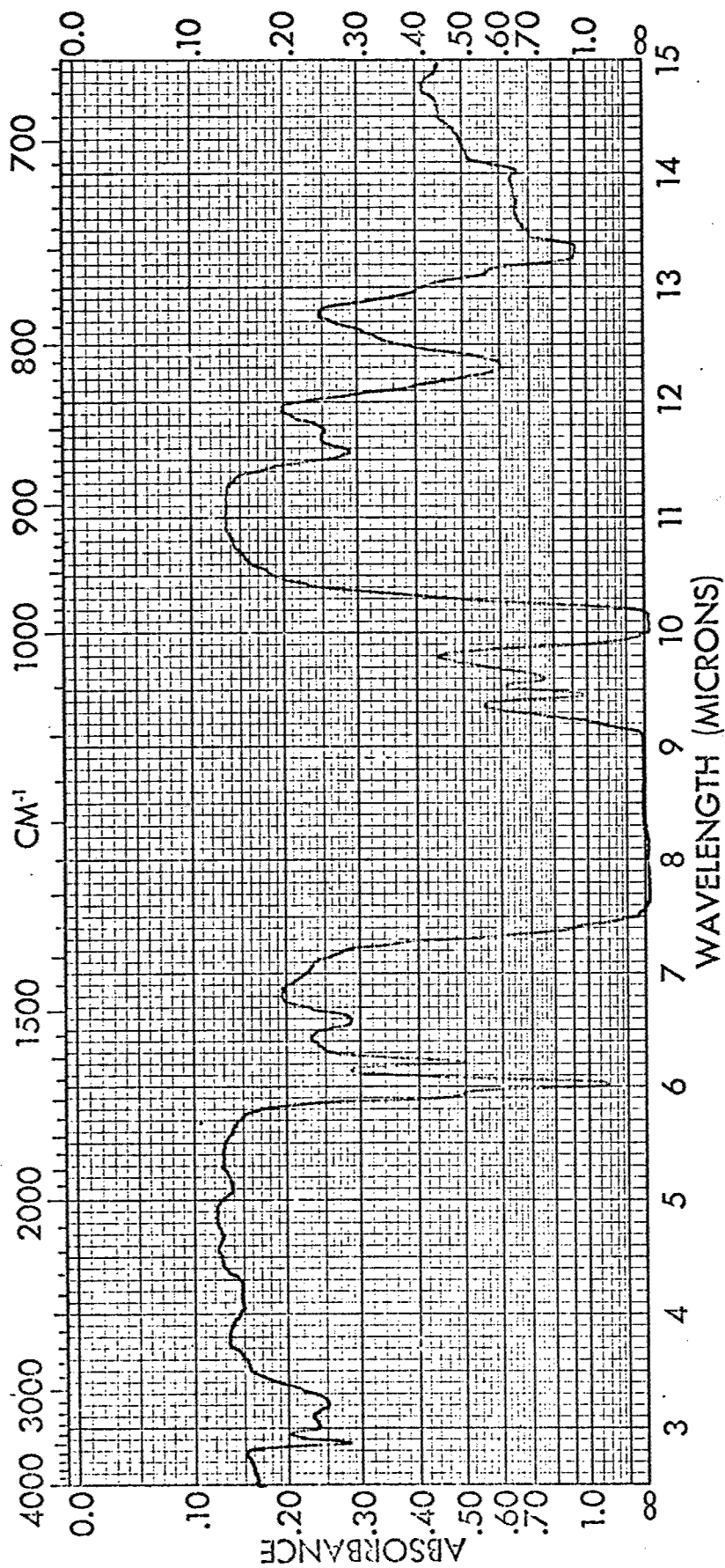


Figure 16.

An Infrared Spectrum of a Mixture of  
 $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{C}(=\text{NH})\text{NH}_2$  and  
 $[\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}(\text{CF}_3)\text{CNH}]_2\text{NH}$  (liquid)

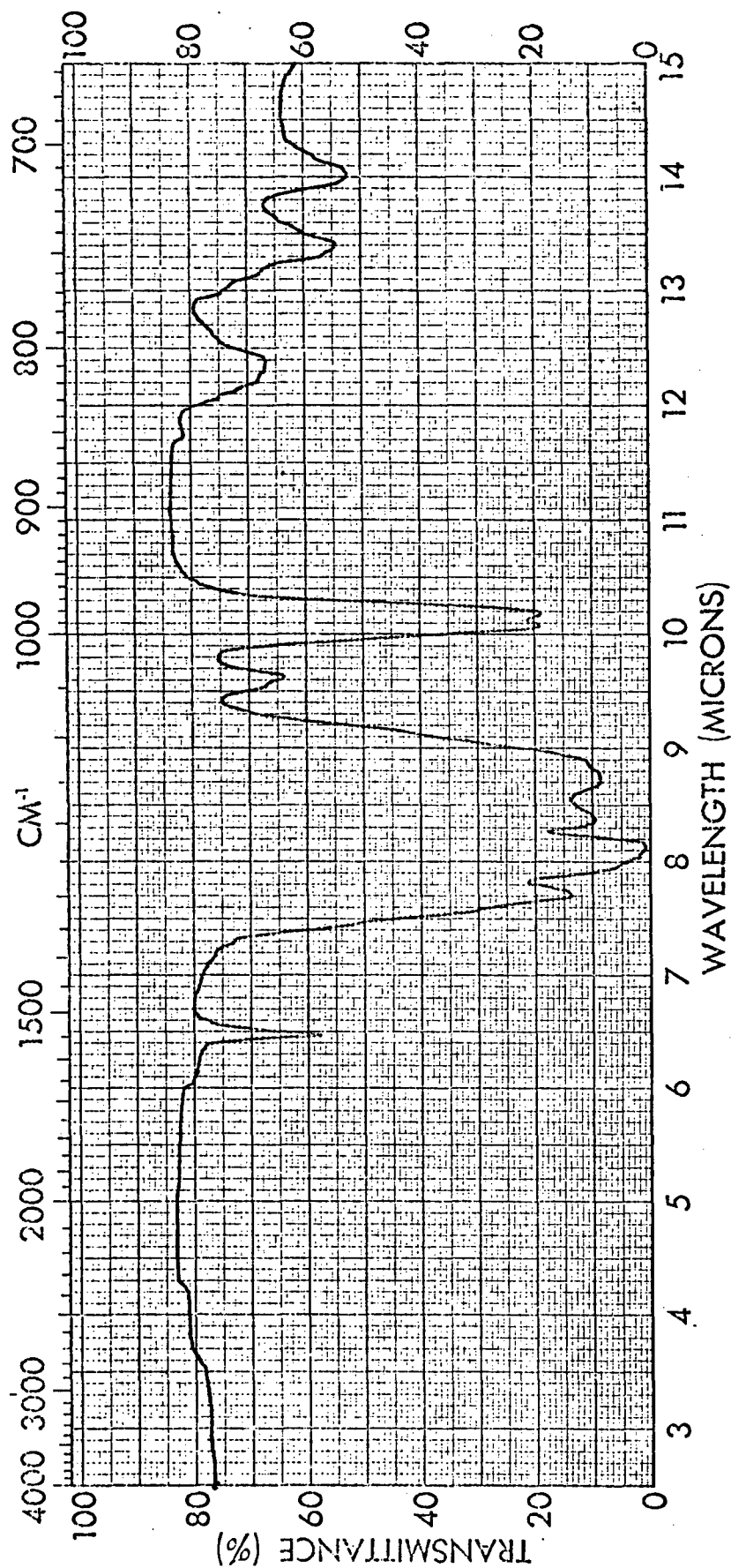


Figure 17.

An Infrared Spectrum of  
 $[C_3F_7O[CF(CF_7)CF_2O]_3CF(CF_3)CN]_3$   
s-Triazine Fluid